



# Infrared Spectroscopy

## CHAPTER

# 13

ONE OF THE MAJOR TASKS that an organic chemist faces in the laboratory is the determination of the structure of an unknown compound. This could be a compound isolated from a reaction mixture or a sample of a suspected illicit drug. In these cases the chemist usually has some idea of what the structure might be. Or it could be a compound isolated from a plant or animal source, in which case the information concerning its structure may be quite limited. In the not too distant past, the determination of the structure of such a compound was an enormous task, sometimes requiring years of work. The general procedure was to submit the unknown to numerous different chemical reactions. Each of these reactions supplied a little more information about the structure. Eventually, like a jigsaw puzzle, the structure was assembled. A simple example of this process, using the ozonolysis reaction, was described in Section 11.11.

Today, organic chemists rely on an array of very powerful instruments that enable them to identify compounds in much less time. With use of these instruments, it is often possible to determine the structure of an unknown compound in less than an hour. Three of the most powerful techniques are presented in this and the following chapters. They are infrared spectroscopy and two related techniques: proton and carbon-13 nuclear magnetic resonance spectroscopy. **Spectroscopy** is the study of the interaction of electromagnetic radiation (light) with molecules.

This chapter begins with a discussion of electromagnetic radiation and spectroscopy in general. Then infrared spectroscopy is presented. We will learn how the functional groups that are present in a compound can be identified by examination of its infrared spectrum. In the next chapter, we will see how nuclear magnetic resonance spectroscopy complements infrared spectroscopy by pro-

### MASTERING ORGANIC CHEMISTRY



- ▶ Predicting the Important Absorption Bands in an Infrared Spectrum
- ▶ Determining the Functional Group of a Compound from Its IR Spectrum

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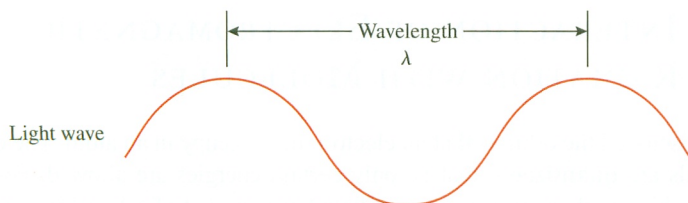
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viding information about the hydrocarbon part of the compound. A combination of these techniques often provides enough information for the identification of an unknown.

## 13.1 ELECTROMAGNETIC RADIATION

Electromagnetic radiation is a general term for light, not just the visible light that our eyes detect but many other types also, including infrared, ultraviolet, and microwave. You are probably aware that light has properties of both particles and waves. Light is characterized by its **wavelength**,  $\lambda$ , which is the distance of one complete cycle of the light wave, that is, the distance between successive crests (or troughs) of the wave. Wavelength has units of length, such as centimeter and nanometer.



Light is also characterized by its **frequency**,  $\nu$ , which is the number of wave cycles that pass a point in a second. The unit for frequency is seconds<sup>-1</sup> (s<sup>-1</sup>), also called cycles per second or hertz (Hz). The product of the wavelength times the frequency equals the speed of light ( $c$ ):

$$\lambda \nu = c = 3.00 \times 10^8 \text{ m s}^{-1}$$

The energy of one light photon ( $\epsilon$ ) is equal to the frequency times Planck's constant or Planck's constant times the speed of light divided by the wavelength:

$$\epsilon = h\nu = hc/\lambda$$

$h$  = Planck's constant =  $1.58 \times 10^{-37}$  kcal s ( $6.63 \times 10^{-37}$  kJ s)

You have probably begun to remember some energy values in units of kcal/mol (or kJ/mol). For example, typical covalent single-bond strengths are in the range of 50 to 100 kcal/mol (210–420 kJ/mol), and the amount of thermal energy available at room temperature is about 20 kcal/mol (84 kJ/mol). For comparison purposes, therefore, it is more convenient to use the energy of a mole of photons ( $E$ ) in units of kcal/mol (or kJ/mol). This requires that  $\epsilon$  be multiplied by Avogadro's number ( $N = 6.02 \times 10^{23} \text{ mol}^{-1}$ ). The appropriate equations then become in units of kcal/mol:

$$E = (9.53 \times 10^{-14} \text{ s kcal/mol})(\nu)$$

or  $E = (2.86 \times 10^{-5} \text{ m kcal/mol})(1/\lambda)$

and in units of kJ/mol:

$$E = (3.99 \times 10^{-13} \text{ s kJ/mol})(\nu)$$

or  $E = (1.20 \times 10^{-4} \text{ m kJ/mol})(1/\lambda)$



where the frequency,  $\nu$ , is in units of  $\text{s}^{-1}$  or the wavelength,  $\lambda$ , is in units of meters (m). It is important to remember that the energy of light is directly proportional to its frequency and inversely proportional to its wavelength.

Low-Energy Light	High-Energy Light
Low frequency	High frequency
Long wavelength	Short wavelength

### PROBLEM 13.1

Calculate these quantities:

- The wavelength of light (in centimeters) with a frequency of  $9.00 \times 10^{12}$  Hz.
- The frequency of light with a wavelength of 310 nm.
- The energy of light (in kcal/mol or kJ/mol) with a frequency of  $9.00 \times 10^{12}$  Hz.
- The energy of light (in kcal/mol or kJ/mol) with a wavelength of 310 nm.

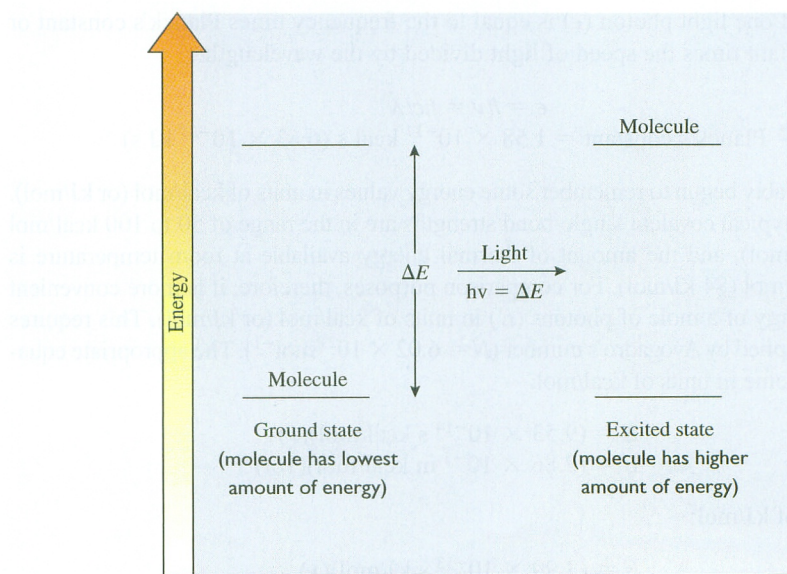
## 13.2 INTERACTION OF ELECTROMAGNETIC RADIATION WITH MOLECULES

Chapter 3 discussed the orbitals that an electron may occupy in an atom. The energies of these orbitals are **quantized**—that is, only certain energies are allowed. For example, there is no orbital with an energy intermediate between that of a  $1s$  orbital and that of a  $2s$  orbital. Not only are the energies of the electron orbitals quantized, but all of the energy states of a molecule are quantized. It is this fact that makes spectroscopy possible.

To illustrate, let's consider a hypothetical molecule that has only two energy states (see Figure 13.1). Initially, the molecule has the lower amount of energy—it is in the **ground state**. When the molecule interacts with light that has an energy exactly equal

Figure 13.1

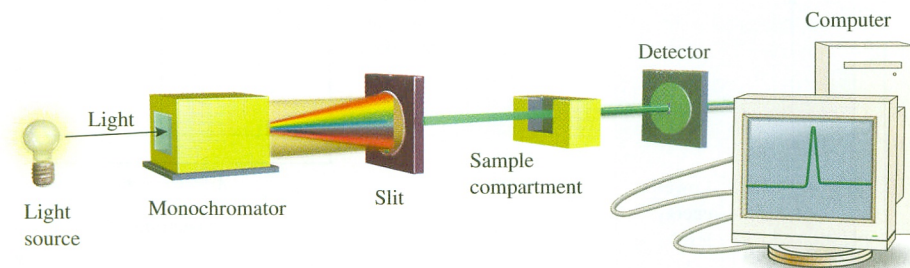
TWO ENERGY STATES OF A  
HYPOTHETICAL MOLECULE.





to the energy difference between the two states—that is, light with a frequency such that  $h\nu = \Delta E$ —the molecule absorbs the light and is raised to the higher-energy state, known as an **excited state**. If the energy of the light does not match the energy difference between the two states, then the light is not absorbed. A **spectrum** is just a plot of the amount of light that is absorbed versus the frequency (or wavelength) of the light. The spectrum provides information about the spacing of the energy levels of the molecule. Because these energy levels depend on the structure of the molecule, this information can, with practice, be used to determine the structure of the compound.

The following is a simplified schematic representation of an absorption spectrometer:



Light from an appropriate source is passed through a monochromator. A monochromator is a device, such as a prism, that spreads or disperses the light into its various wavelengths. The light from the monochromator is then passed through the sample of the compound under investigation to see which wavelengths of light are absorbed by the sample. A detector is used to determine the intensity at each wavelength, and the results are sent to a recorder that plots the spectrum. Today, this entire process of gathering and storing the data and plotting the resulting spectrum is usually computerized.

In some types of spectroscopy there are only a few, well-separated energy levels. In such cases, only a very narrow range of wavelengths is absorbed each time the molecule is excited from its lowest-energy state to some higher-energy state, resulting in an absorption line for each of these transitions. The spectrum consists of a number of these absorption lines. More commonly, however, there are a number of energy sublevels in each energy state. In such cases a number of closely spaced wavelengths are absorbed. The lines are often so close together that they cannot be resolved and the absorption appears as a broad peak or band. Figure 13.2 illustrates both of these situations.

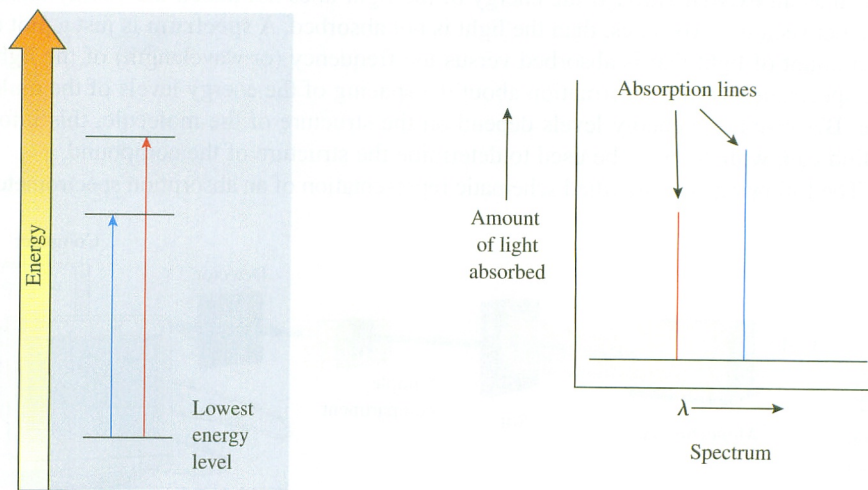
## 13.3 THE ELECTROMAGNETIC SPECTRUM

The spectrum of electromagnetic radiation, ranging from very energetic cosmic rays to low-energy radio waves, is shown in Figure 13.3. The energy of cosmic and gamma radiation is so large that this radiation passes right through most matter because there are no states separated by enough energy that these high-energy photons can be absorbed. However, most other types of radiation are absorbed, resulting in the formation of a variety of different excited states.

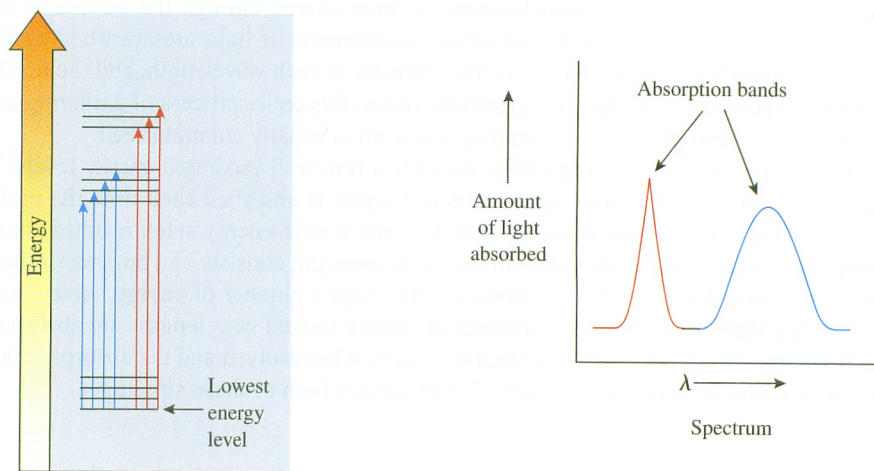
The types of spectroscopy that are of most use to organic chemists employ infrared light or radiation in the radio region. Light in the infrared region has energy that



- a When there are only a few energy levels and the spacing between them is large enough, a line spectrum is produced.



- b When there are many, closely spaced sublevels in each energy level, the absorptions occur in broad bands because the individual lines are not resolved.



**Figure 13.2**

**TYPES OF ABSORPTION SPECTRA: a LINE SPECTRUM AND b BROADBAND SPECTRUM.**

matches the energy separation of the vibrational energy states of covalent bonds. An infrared spectrum provides information about the types of bonds and therefore the functional groups that are present in the molecule. Nuclear magnetic resonance spectroscopy employs very low energy radiation in the radio region. It involves transitions between nuclear spin states and provides information about the hydrogens and carbons in the molecule.



Cosmic and gamma rays are very high energy and do not interact much with matter because no energy states with  $\Delta E$  this large are available. The energy of X-rays corresponds to  $\Delta E$  between electron shells and can excite and eject inner-shell electrons.

Light from the ultraviolet and visible regions has the correct energy to excite electrons from bonding or nonbonding MOs to antibonding MOs in some molecules. An example of such an electronic transition is the excitation of an electron in a bonding pi MO to an antibonding pi MO. Ultraviolet and visible spectroscopy is useful in organic chemistry and is discussed in Chapter 15.

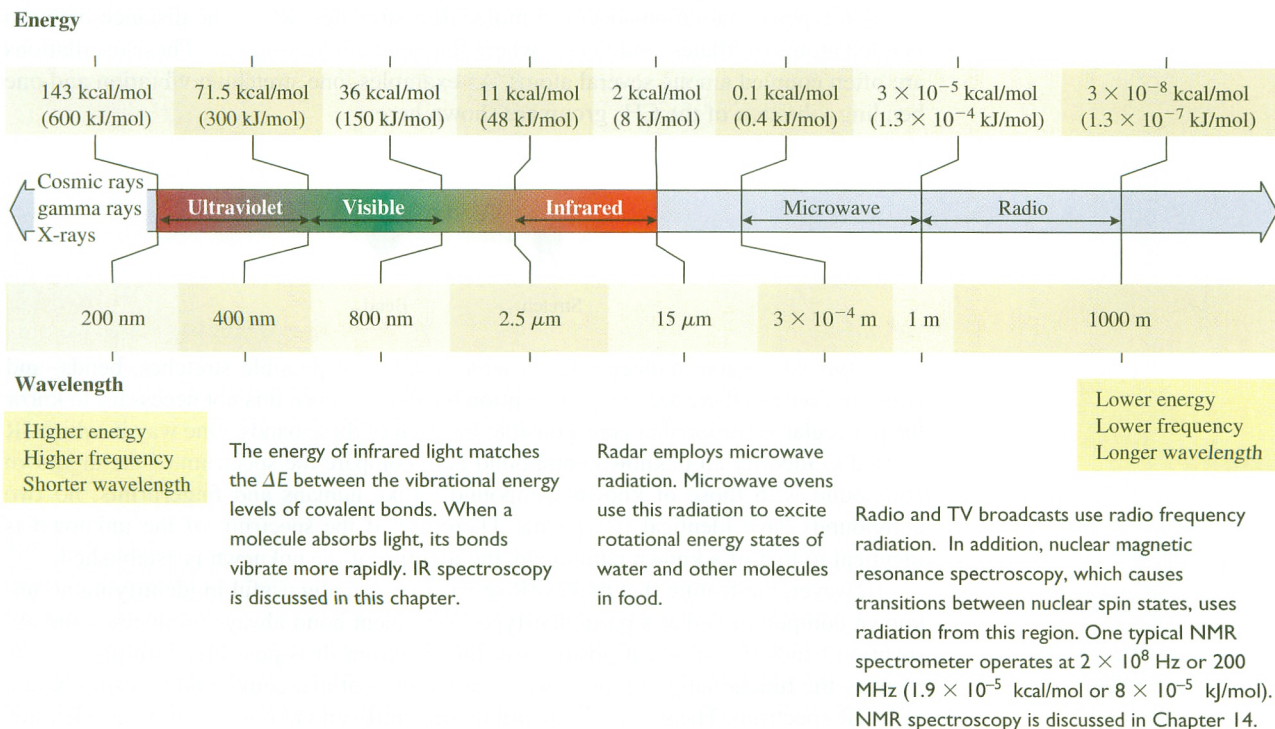


Figure 13.3

#### THE ELECTROMAGNETIC SPECTRUM.

#### PROBLEM 13.2

What kind of light has a frequency of  $9.00 \times 10^{13}$  Hz?

#### PROBLEM 13.3

Some NMR spectrometers operate at  $4 \times 10^8$  Hz (400 MHz). What is the energy of this radiation?

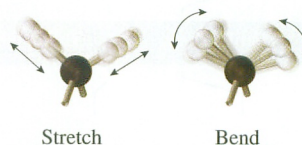
## 13.4 INFRARED SPECTROSCOPY

The atoms of a covalent bond never sit still, even at absolute zero. They are constantly vibrating, somewhat like balls connected by springs. The energies of the vibrations, like all energies on a molecular scale, are quantized. At room temperature, most molecules are in the lowest vibrational energy level. The separation between the energy levels



ranges from 1 to 14 kcal/mol (4–60 kJ/mol). This energy corresponds to the energy of infrared (IR) radiation. Therefore, when IR radiation is passed through a sample of a compound, the light is absorbed and the molecule is excited to a higher vibrational state when the energy of the light matches the energy separation between two vibrational energy levels. Because each vibrational level has a number of closely spaced rotational energy levels, IR absorptions appear as bands rather than lines.

Two types of vibrations occur in molecules: stretches, where the distance between bonded atoms oscillates, and bends, where the bond angles oscillate. These oscillations are often coupled among several atoms. As examples, one stretching vibration and one bending vibration of the  $\text{CH}_2$  group are shown here:



A typical organic molecule has a large number of possible stretches, bends, and combinations, so there are many absorption bands. However, it is not necessary to know the particular vibration that is responsible for each of these bands. One way in which IR is used to identify an unknown compound is to compare the spectrum of the unknown compound with those of known compounds. Like humans and fingerprints, no two compounds have identical IR spectra. Therefore, if the spectrum of the unknown is identical to that of a known compound, the identity of the unknown is established.

However, the feature that makes IR spectroscopy really useful in identifying an unknown compound is that a particular type of covalent bond always produces some absorption bands in consistent positions in the spectrum. It is possible, with practice, to identify the functional group or groups that are present in a compound by examination of its IR spectrum. Therefore, it is possible to identify an unknown sample as a ketone, or ester, or alcohol, for example, just by examination of its IR spectrum.

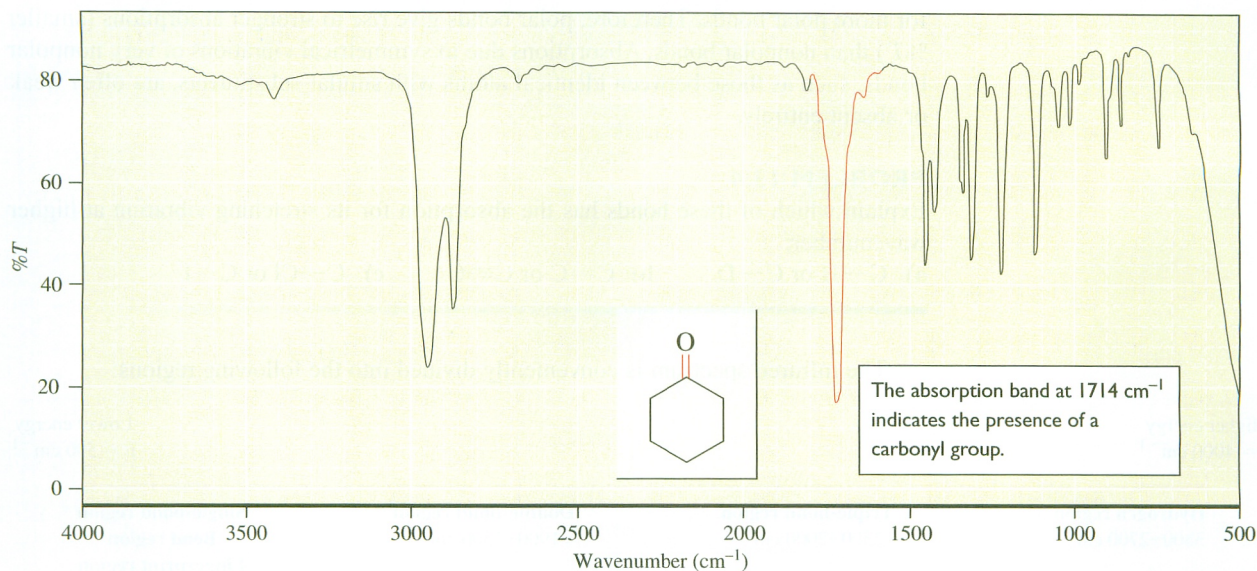
Figure 13.4 shows a typical IR spectrum, that of cyclohexanone. The percentage of light transmitted (percent transmittance, % $T$ ) is plotted on the  $y$ -axis, with 100% transmittance (no light absorbed) at the top of the spectrum. Absorption bands therefore come downward from the top of the spectrum. The intensity of a band is often described qualitatively as w (weak, high % $T$ ), m (medium), or s (strong, low % $T$ ). The positions of the absorption bands are usually expressed as wavenumbers ( $\bar{\nu}$ ), rather than wavelengths or frequencies. The **wavenumber**, whose unit is  $\text{cm}^{-1}$ , is the reciprocal of wavelength:

$$\bar{\nu} = 1/\lambda$$

Note that wavenumbers are directly proportional to energy; that is, light of higher wavenumber has higher energy. The wavenumber range covered in most of the IR spectra in this book is from  $4000\text{ cm}^{-1}$  (higher energy) to  $500\text{ cm}^{-1}$  (lower energy).

To give a brief preview of how IR spectroscopy is useful, note the strong absorption band at  $1714\text{ cm}^{-1}$  in the spectrum of cyclohexanone (Figure 13.4). This band is due to the presence of the carbonyl group. As we will see shortly, all compounds that have a carbonyl group show a similar absorption in the general region of  $1700\text{ cm}^{-1}$ . Therefore, the presence of such an absorption band in the spectrum of an unknown compound is strong evidence that the unknown has a carbonyl group.





Percent transmittance (%T) is plotted along the y-axis with 100% T at the top. Absorption bands come down from the top of the spectrum.

Wavenumber, in units of  $\text{cm}^{-1}$ , is plotted along the x-axis. The IR spectrometer that was used to obtain this spectrum covers the region from 4000 to 500  $\text{cm}^{-1}$ .

**Figure 13.4**

THE INFRARED SPECTRUM OF CYCLOHEXANONE.

## 13.5 GENERALIZATIONS

An approximate value for the wavenumber for a particular IR transition can be calculated from the following equation:

$$\text{wavenumber} = \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{M}}$$

where  $k$  is the force constant for the bond and  $M$  is the reduced mass of the bonded atoms. The force constant,  $k$ , is related to the bond strength and is larger for stronger bonds. It is also larger for bond-stretching vibrations than for bending vibrations. The reduced mass,  $M$ , is larger for atoms of larger atomic mass. On the basis of this information the following generalizations about the position of an absorption can be made:

1. Because of their larger force constants, stronger bonds absorb at higher wavenumbers than weaker bonds.
2. For similar reasons, bond stretches absorb at higher wavenumbers than bends.
3. Bonds involving a light hydrogen atom have smaller reduced masses and therefore absorb at higher wavenumbers than bonds involving only heavier atoms.

For IR energy to be absorbed and result in a transition between vibrational energy levels, the dipole moment of the molecule must change as the vibration occurs. The intensity of the absorption is proportional to the magnitude of this change and is larger



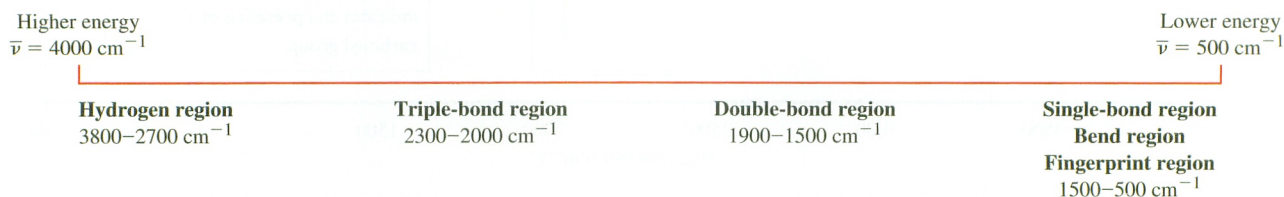
for more polar bonds. Therefore, polar bonds give rise to stronger absorptions (smaller %*T*) than nonpolar bonds. Absorptions due to symmetrical vibrations of very nonpolar bonds, such as those between identical atoms with similar substituents, are often weak or absent entirely.

### PROBLEM 13.4

Explain which of these bonds has the absorption for its stretching vibration at higher wavenumber:

- a) C—H or C—D      b) C=C or C≡C      c) C—Cl or C—I

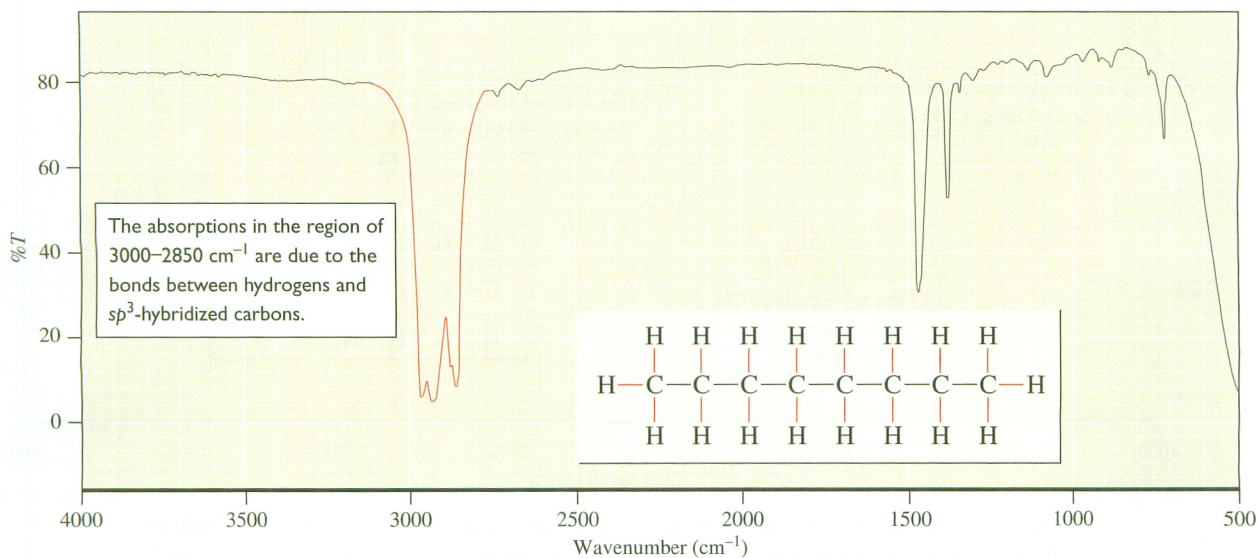
The infrared spectrum is conveniently divided into the following regions:



The highest-energy region, from 3800 to 2700  $\text{cm}^{-1}$ , is called the **hydrogen region**. Absorptions due to O—H, N—H, and C—H bond stretches occur here. These absorption bands are very high in energy because hydrogen is such a light atom. All of the bonds involving only heavier atoms, such as C—C and C—O bonds, absorb at lower energies. Next comes the **triple-bond region**, from 2300 to 2000  $\text{cm}^{-1}$ . Absorptions due to CN and CC triple-bond stretches occur here. These are the strongest bonds, so they occur at higher wavenumber than double and single bonds. The **double-bond region**, from 1900 to 1500  $\text{cm}^{-1}$ , is lower in energy because double bonds are weaker than triple bonds. Absorptions due to CO, CN, and CC double-bond stretches occur in this region. Finally, at lowest energy is the **single-bond region**, from 1500 to 500  $\text{cm}^{-1}$ . In addition to the absorptions due to stretches of single bonds, absorptions due to bends also occur in this region. There are usually so many bands here that it is difficult to assign each to a specific vibration. However, the large number of bands make this region especially useful in comparing spectra, so it is also known as the **fingerprint region**. Let's consider each of these regions in more detail.

## 13.6 THE HYDROGEN REGION

Bonds between a light hydrogen atom and oxygen, nitrogen, and carbon atoms have absorptions in this region. The position of the band depends on the bond strength, which increases in the order C—H < N—H < O—H. The absorptions for C—H bonds appear at lower energy, in the region of 3330 to 2700  $\text{cm}^{-1}$ . The C—H bond strength varies slightly because of the hybridization of the carbon atom, increasing in the order  $\text{H}-\text{C}_{sp^3} < \text{H}-\text{C}_{sp^2} < \text{H}-\text{C}_{sp}$ . The absorptions for a bond between a hydrogen and an  $sp^3$ -hybridized carbon appears in the region of 3000 to 2850  $\text{cm}^{-1}$ . Most



**Alkanes:** Most compounds have an alkyl part and therefore have absorption bands in the 3000–2850  $\text{cm}^{-1}$  region due to their CH bonds. The feature that distinguishes alkanes is the absence of bands for hydroxy groups, carbonyl groups, and so on. The spectrum of an alkane usually has many fewer absorptions than those of compounds with other functional groups.

**Figure 13.5**

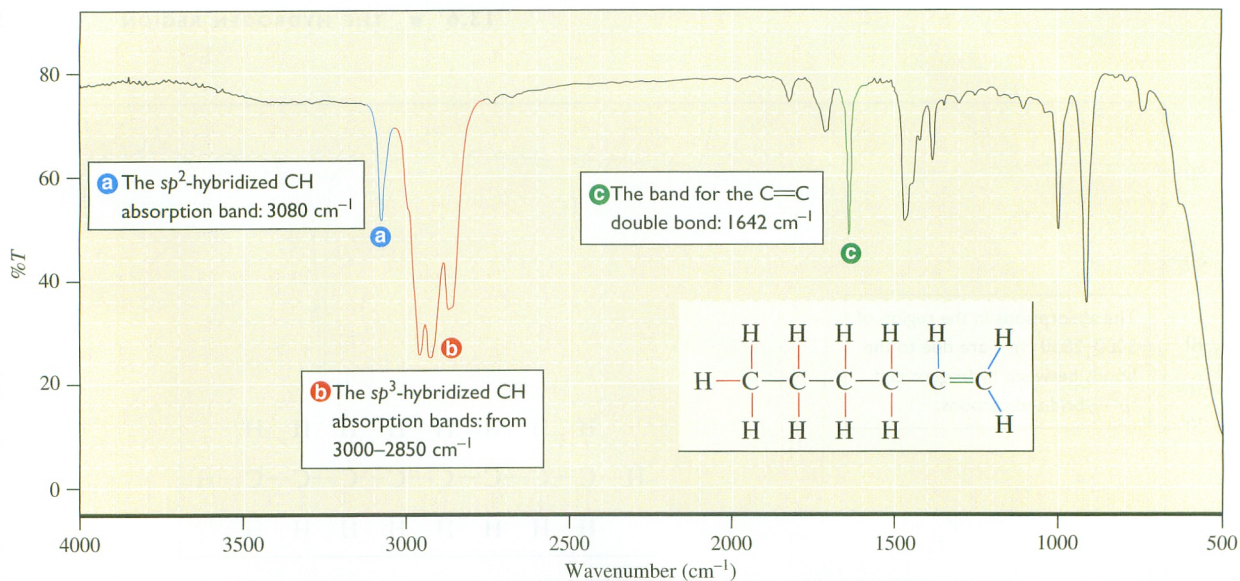
**THE INFRARED SPECTRUM OF OCTANE.**

organic compounds have several bands in this region, owing to the numerous C—H bonds of this type. Although these bonds are not very polar, the absorptions are relatively strong because of the number of bonds. An example is provided in the spectrum of octane, shown in Figure 13.5. For now, do not attempt to identify all of the absorption bands when you examine the IR spectra in these figures. Instead, focus on the particular part of the spectrum that is currently being discussed—that is, the absorption due to the C—H bonds in this particular spectrum. Most of the spectra have additional bands identified. Subsequent sections will refer back to these bands. In addition, each spectrum has a summary of the absorptions due to the particular functional group illustrated by that spectrum. Later, we will return to examine all of the important bands in each of these spectra.

The bond between a hydrogen and an  $\text{sp}^2$ -hybridized carbon is somewhat stronger than that between a hydrogen and an  $\text{sp}^3$ -hybridized carbon and thus appears at higher wavenumbers, in the region of 3100 to 3000  $\text{cm}^{-1}$ . Note that 3000  $\text{cm}^{-1}$  is a convenient dividing line for alkene and alkane C—H absorptions. The spectrum of 1-hexene, shown in Figure 13.6, shows bands for both types of hydrogens.

The strongest C—H bond is that of a 1-alkyne, where the hydrogen is bonded to an  $\text{sp}$ -hybridized carbon. Therefore, the C—H stretch of a 1-alkyne occurs at the highest wavenumber of all C—H bonds, near 3300  $\text{cm}^{-1}$ . The spectrum of 1-hexyne is shown in Figure 13.7.



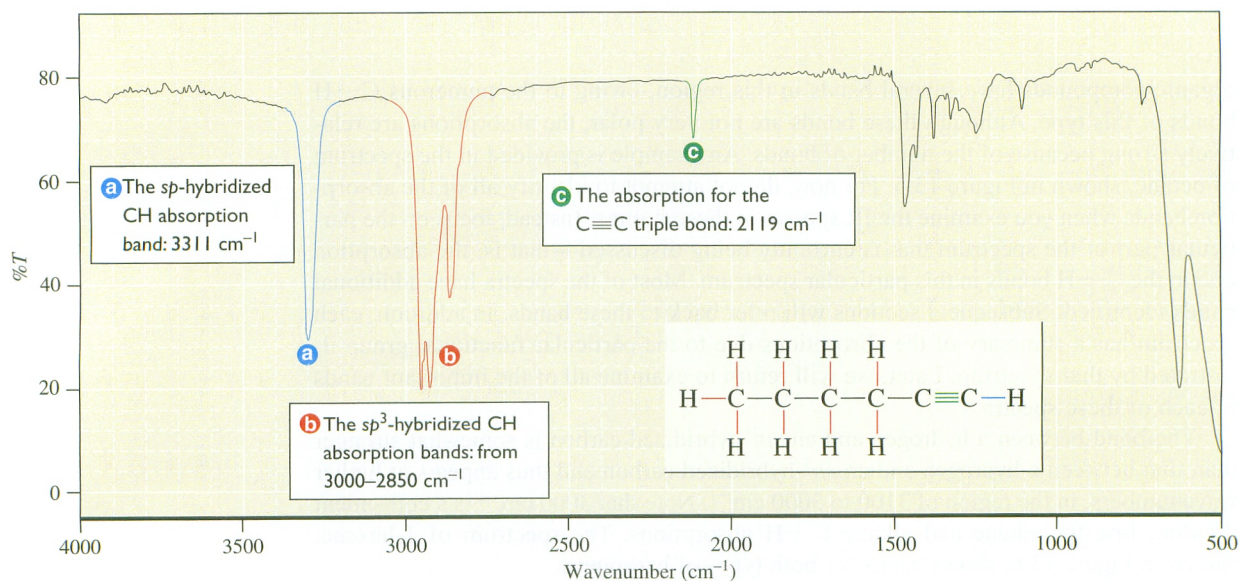


The bands for hydrogens bonded to  $sp^2$ -hybridized carbons appear at wavenumbers just greater than 3000 cm<sup>-1</sup>. The bands for hydrogens bonded to  $sp^3$ -hybridized carbons appear at wavenumbers just less than 3000 cm<sup>-1</sup>.

**Alkenes:** Most alkenes have absorption bands in the 3100–3000 cm<sup>-1</sup> region, due to the CH bonds where the carbon is  $sp^2$  hybridized, and an absorption in the 1660–1640 cm<sup>-1</sup> region due to the CC double bond. However, the CH absorption is absent if the double bond is tetrasubstituted. Furthermore, the CC double-bond absorption is often weak because the bond is not very polar and may be difficult to discern.

**Figure 13.6**

THE INFRARED SPECTRUM OF 1-HEXENE.

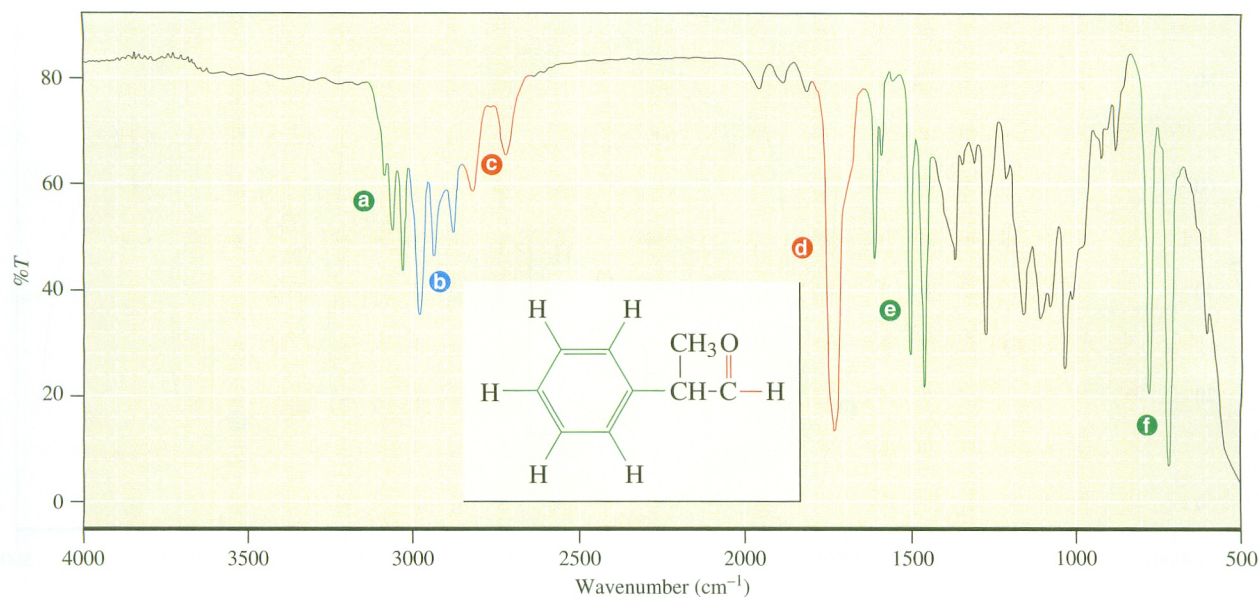


**Alkynes:** Terminal alkynes, where the triple bond occurs at the end of a carbon chain, are readily identified by a band near 3300 cm<sup>-1</sup> due to the bond between the hydrogen and the  $sp$ -hybridized carbon and a band in the region of 2150–2100 cm<sup>-1</sup> due to the CC triple bond. Alkynes in which the triple bond is in the middle of a carbon chain are more difficult to recognize because the CH bond is absent and the band due to the triple bond may be quite weak.

**Figure 13.7**

THE INFRARED SPECTRUM OF 1-HEXYNE.





Three different types of CH bonds can be detected in this spectrum:

**a**  $\text{sp}^2$ -hybridized CH bonds ( $3100\text{--}3000\text{ cm}^{-1}$ )

**b**  $\text{sp}^3$ -hybridized CH bonds ( $3000\text{--}2850\text{ cm}^{-1}$ )

**c** Aldehyde CH bond (two bands at  $2820$  and  $2720\text{ cm}^{-1}$ )

**d** The absorption for the carbonyl group of the aldehyde:  $1724\text{ cm}^{-1}$

**e** The bands due to the aromatic ring skeletal vibrations:  $1602$ ,  $1580$ ,  $1493$ , and  $1450\text{ cm}^{-1}$

**f** The bands due to the CH bending vibrations of the aromatic ring:  $760$  and  $700\text{ cm}^{-1}$

**Aldehydes:** The appearance of two bands in the region of  $2830\text{--}2700\text{ cm}^{-1}$  (hydrogen to carbonyl carbon bond) and the presence of an absorption due to a carbonyl group provide evidence for the presence of an aldehyde. The band for the carbonyl of an aldehyde occurs near  $1730\text{ cm}^{-1}$ , although it is shifted to lower wavenumbers when conjugated.

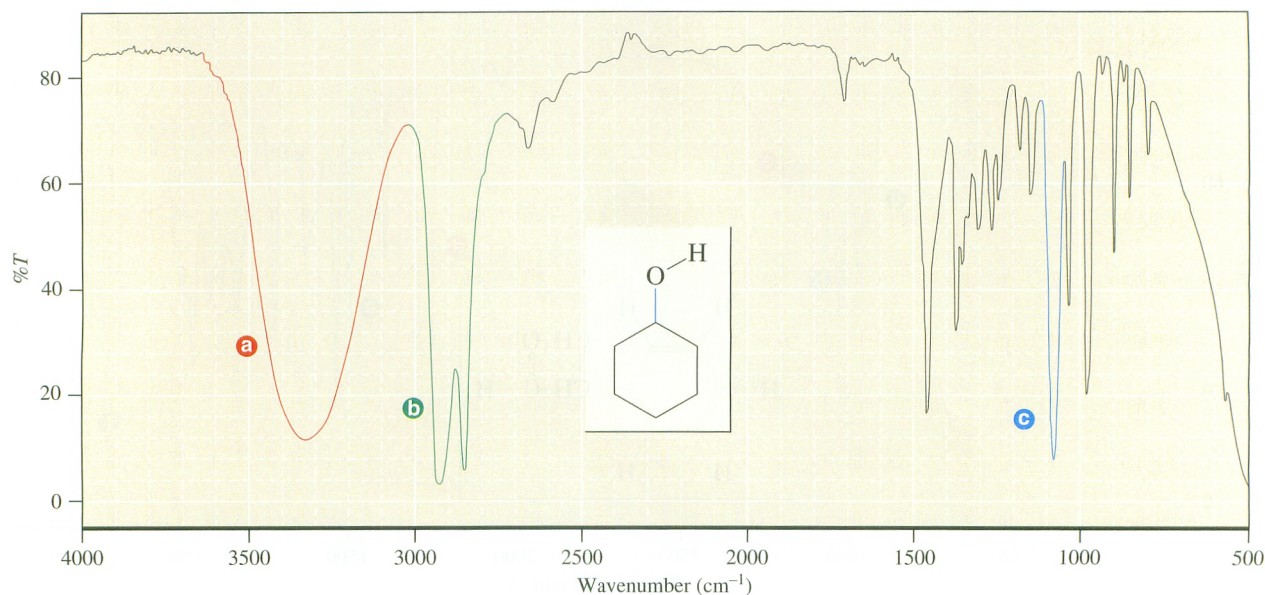
Figure 13.8

#### THE INFRARED SPECTRUM OF 2-PHENYLPROPANAL.

Finally, the C—H bond between the carbonyl carbon and hydrogen of an aldehyde normally results in two absorptions in the region of  $2830$  to  $2700\text{ cm}^{-1}$  and can usually be distinguished from the alkane C—H absorptions. Three different types of absorptions due to C—H bonds can be seen in the spectrum of 2-phenylpropanal shown in Figure 13.8.

An O—H bond is stronger than a C—H bond, so its absorption band appears at higher energy, in the region of  $3600\text{ cm}^{-1}$ . However, a band at this position for a hydroxy group is observed only in the vapor phase or in very dilute solution, where intermolecular hydrogen bonding between O—H groups is negligible. Most IR spectra are not run under such conditions. Instead, the samples are considerably more concentrated, often even pure (also termed neat) liquids. Under these conditions, hydrogen bonding is very important and weakens the O—H bond, causing the absorption to shift to lower wavenumbers, from  $3550$  to  $3200\text{ cm}^{-1}$ . The band is very broad because the strength of each hydrogen bond differs slightly, depending on the exact separation and geometry of





**a** The absorption band for the OH bond:  $3332\text{ cm}^{-1}$ . Note how broad this band is compared to other bands in the spectrum.

**b** The  $\text{sp}^3$ -hybridized CH absorption bands: from  $3000\text{--}2850\text{ cm}^{-1}$

**c** The CO stretching vibration:  $1067\text{ cm}^{-1}$

**Alcohols:** Alcohols are characterized by a strong and very broad absorption in the  $3550\text{--}3200\text{ cm}^{-1}$  region due to the hydrogen-bonded OH group. They also show a strong band for the CO bond in the  $1300\text{--}1000\text{ cm}^{-1}$  region, although this absorption can be difficult to identify because it occurs in the fingerprint region with many other bands.

**Figure 13.9**

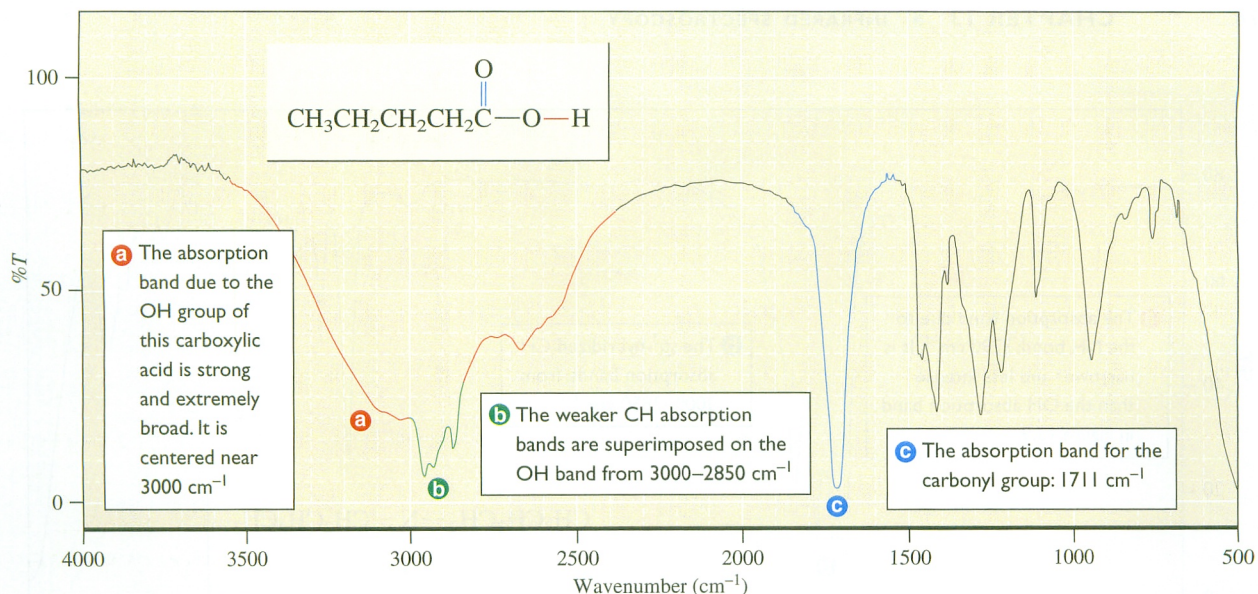
THE INFRARED SPECTRUM OF CYCLOHEXANOL.

the two partners. Because the O—H bond is quite polar, this absorption is very strong. Figure 13.9 shows the IR spectrum of cyclohexanol. The band for the O—H occurs at  $3332\text{ cm}^{-1}$ . Note that this band is considerably broader than the other bands in the spectrum.

Because a carboxylic acid forms very strong hydrogen bonds, the band for its O—H group is extremely broad and occurs at even lower wavenumbers, usually centered near  $3000\text{ cm}^{-1}$ . This band overlaps the C—H absorptions but is readily distinguished from them because it is so broad. As illustrated in Figure 13.10, the C—H absorptions can often be seen superimposed on the intense O—H absorption.

The N—H bond strength is between those of O—H and C—H bonds, so it absorbs between these two groups, in the region of  $3400\text{ to }3250\text{ cm}^{-1}$ . Like the O—H absorption, it is broadened because of hydrogen bonding, but to a lesser extent because its hydrogen bonds are weaker. Although the region for N—H bands overlaps with the region for O—H bands, with some experience it is usually possible to distinguish the two types because the N—H bands are narrower and less intense than the O—H bands. Primary amines show two bands in this region, whereas secondary amines show only one. Examples are provided in Figures 13.11 and 13.12.

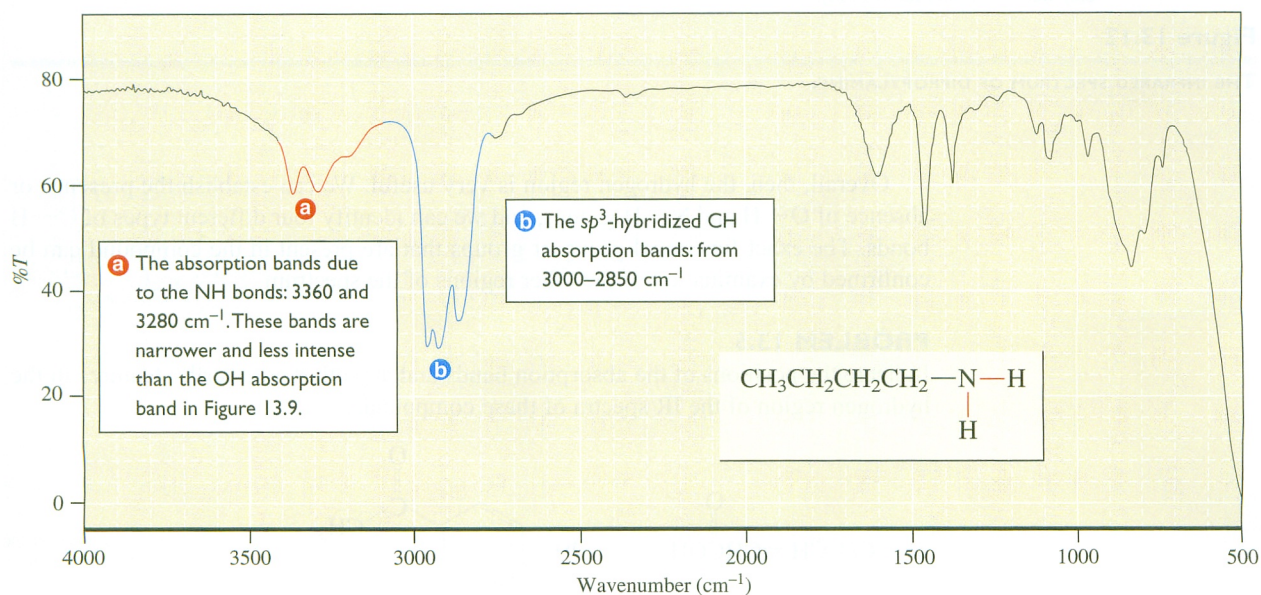




**Carboxylic acids:** A carboxylic acid is readily recognized from its carbonyl absorption, near  $1710\text{ cm}^{-1}$ , and its extremely broad OH band, often centered near  $3000\text{ cm}^{-1}$ . This band is much broader and appears at lower wavenumbers than the OH band of an alcohol. Often, the CH bands are superimposed on the OH absorption of a carboxylic acid.

**Figure 13.10**

THE INFRARED SPECTRUM OF PENTANOIC ACID.

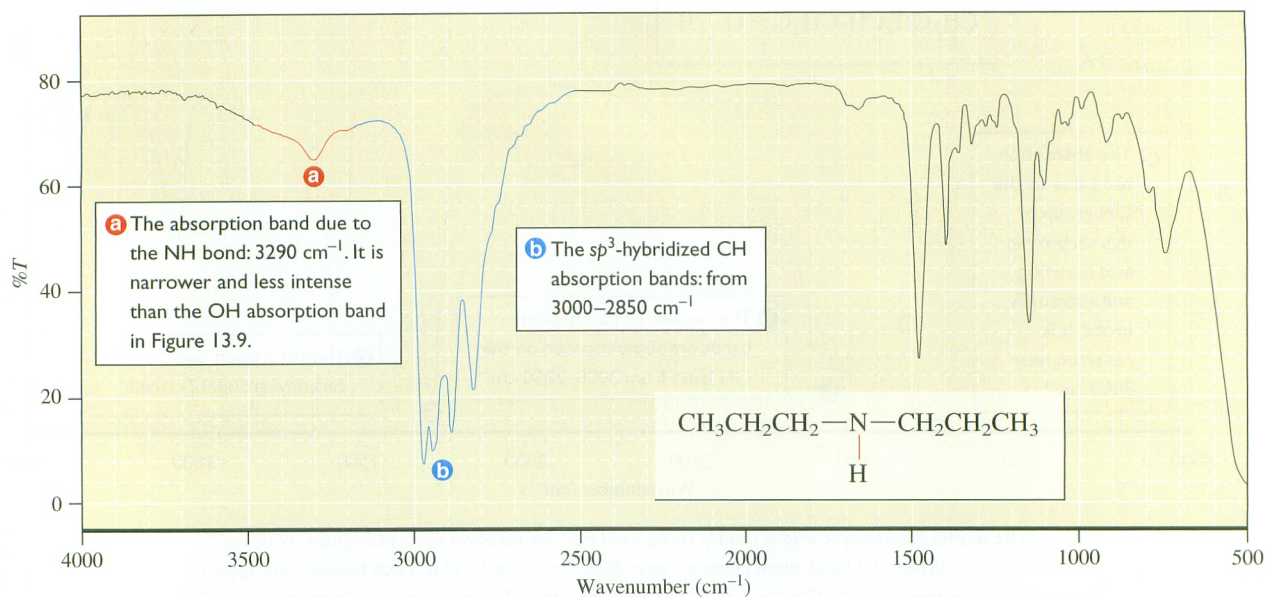


**Primary amines:** Primary amines are characterized by two absorption bands that appear in the  $3400\text{--}3250\text{ cm}^{-1}$  region due to the NH bonds. These absorptions appear in the same region as those due to an OH group but are narrower and less intense. The absorption due to the CN bond stretch is very difficult to use because it occurs in the fingerprint region with only weak to moderate intensity.

**Figure 13.11**

THE INFRARED SPECTRUM OF BUTYLAMINE.





**Secondary amines:** Secondary amines are characterized by an absorption band that appears in the  $3400\text{--}3250\text{ cm}^{-1}$  region due to the NH bond. In contrast to a primary amine, a secondary amine shows only one absorption in this region. Although it appears in the same region as the absorption due to an OH group, it is narrower and less intense so that it can be distinguished with some practice. The absorption due to the CN bond is very difficult to use because it occurs in the fingerprint region with only weak to moderate intensity.

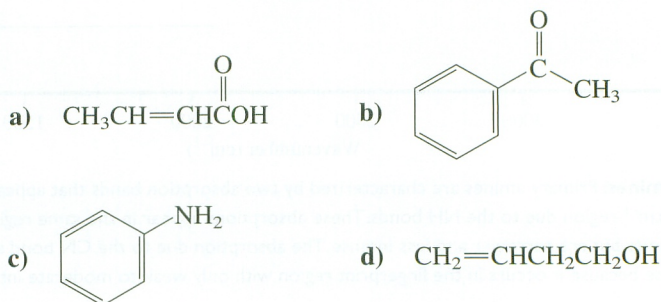
Figure 13.12

THE INFRARED SPECTRUM OF DIPROPYLAMINE.

Overall, then, the hydrogen region is very useful. We can establish the presence or absence of O—H and N—H groups, and we can identify four different types of C—H bonds. The exact functional group or groups that are present in the compound can be confirmed by examination of the other regions of the spectrum.

### PROBLEM 13.5

Indicate the positions of the absorption bands and any other noteworthy features in the hydrogen region of the IR spectra of these compounds:



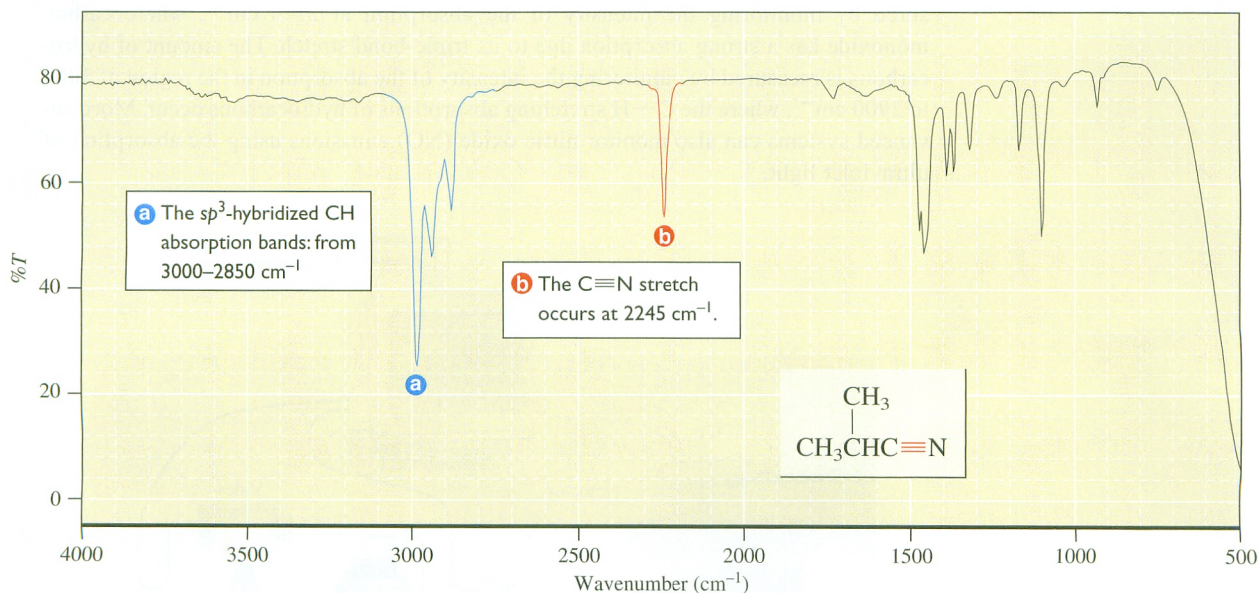


## 13.7 THE TRIPLE-BOND REGION

The large force constant of strong triple bonds results in absorptions in the 2300 to 2000  $\text{cm}^{-1}$  region. The CN triple-bond stretch of a cyano group or nitrile occurs in the region of 2260 to 2220  $\text{cm}^{-1}$ . An example of the absorption band for a CN triple bond is shown in Figure 13.13. The CC triple-bond stretch of an alkyne usually occurs in the region of 2150 to 2100  $\text{cm}^{-1}$ . This band is most visible for 1-alkynes (see Figure 13.7). If the triple bond has similar substituents on the two carbons, the absorption may be very weak or absent altogether because of the lack of change of the dipole moment of the bond during the vibration.

### PROBLEM 13.6

Explain why the presence of a triple bond is much easier to detect in the IR spectrum of 1-hexyne than it is in the spectrum of 3-hexyne.



**Nitriles:** Nitriles are readily identified by the absorption due to the CN triple bond that appears in the region of 2260–2220  $\text{cm}^{-1}$ . This band is relatively strong because the bond is polar.

Figure 13.13

THE INFRARED SPECTRUM OF 2-METHYLPROPANENITRILE.



## Focus On

### Remote Sensing of Automobile Pollutants

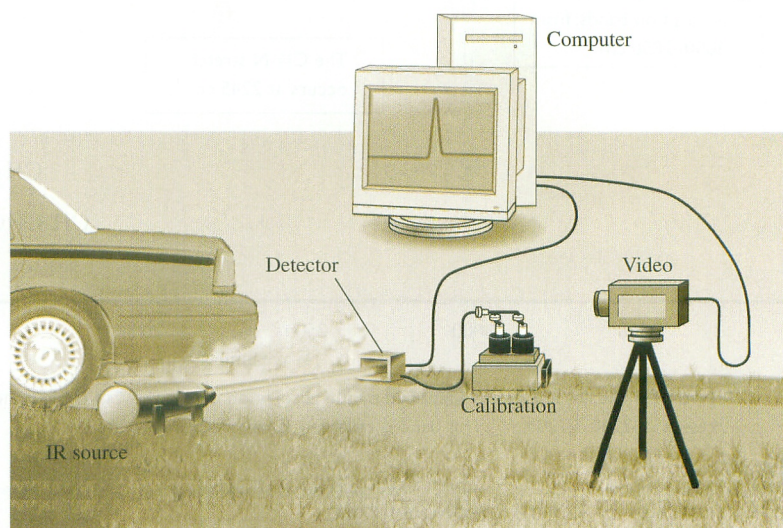
Most types of spectroscopy can be used for quantitative analysis because the intensity of an absorption band—that is, the amount of light absorbed at a particular wavelength—is proportional to the amount of compound in the sample. A group of chemists at the University of Denver has developed a device that can measure the amount of carbon monoxide and hydrocarbons in the exhaust of an automobile by remote sensing—that is, in the street as the automobile passes by.

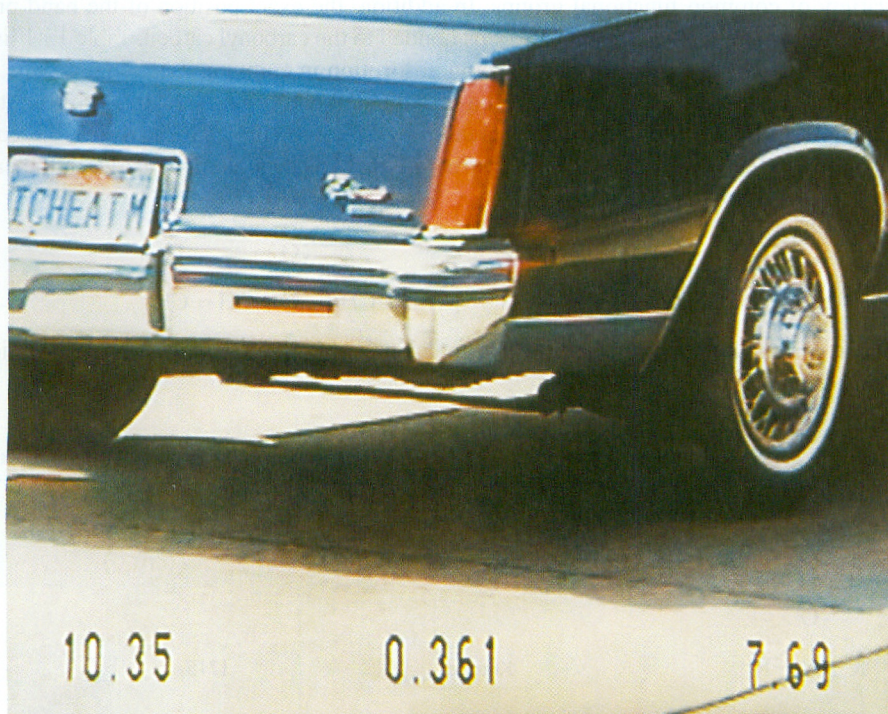
Poorly maintained automobiles pollute by emitting carbon monoxide and hydrocarbons, products of incomplete combustion. Because carbon monoxide is very poisonous and hydrocarbons contribute to the formation of smog, it is desirable to minimize the emission of both of these pollutants.



Carbon monoxide

As shown in the following figure, the remote sensing device consists of a source of IR light on one side of the road and a detector on the other, with the beam at tailpipe height. As the auto passes through the beam, the amount of CO in the exhaust is measured by monitoring the intensity of the absorption at  $2170\text{ cm}^{-1}$ , where carbon monoxide has a strong absorption due to its triple-bond stretch. The amount of hydrocarbons is measured by monitoring the intensity of the absorption in the region of  $3000$  to  $2900\text{ cm}^{-1}$ , where the C—H stretching absorptions of hydrocarbons occur. More advanced systems can also monitor nitric oxide (NO) emissions using the absorption of ultraviolet light.





Prof. Donald Stedman, University of Denver

The amounts of carbon monoxide, hydrocarbons, and carbon dioxide are recorded by a computer, and a video camera records a picture of the license plate of the car. The accompanying picture shows the video screen with the percent CO in the exhaust listed at the lower left, the percent hydrocarbon in the middle, and the percent CO<sub>2</sub> at the right. This particular vehicle was a high polluter, emitting 10.35% CO, 0.36% hydrocarbons, and 7.69% CO<sub>2</sub>. The emission of a well-maintained, low-polluting vehicle contains about 0% CO, 0% hydrocarbons, and 15% CO<sub>2</sub>. Because about 10% of the vehicles emit about 65% of the pollution, the identification and repair of these high polluters could substantially reduce the air pollution caused by automobiles.

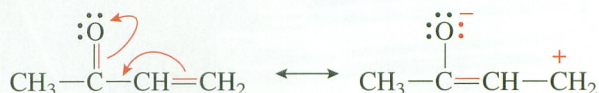
### PROBLEM 13.7

The exhaust from a poorly maintained automobile may contain a wide variety of different hydrocarbon pollutants. Why is the 3000 to 2900 cm<sup>-1</sup> region a good place to monitor the amount of these compounds?



## 13.8 THE DOUBLE-BOND REGION

The double-bond region extends from 1900 to 1500  $\text{cm}^{-1}$ . Carbonyl groups have an absorption band in the general region of 1700  $\text{cm}^{-1}$ . This band is very strong because the CO double bond is very polar and is quite useful because carbonyl groups occur in a variety of common functional groups. In addition, the exact position of the band provides information about the other groups bonded to the carbonyl carbon. Table 13.1 lists the approximate position for the carbonyl absorption in common functional groups. If the carbonyl group is conjugated with a CC double bond or with an aromatic ring, the position of the absorption band is decreased by 20 to 40  $\text{cm}^{-1}$ . This is due to the contribution to the resonance hybrid of a structure that has a single bond between the carbon and the oxygen:



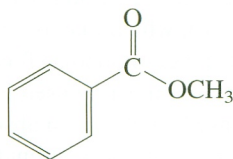
If the carbonyl carbon is part of a five-membered ring, the position of the absorption band is increased by about 30  $\text{cm}^{-1}$ .

**Table 13.1** Infrared Absorption Band Positions of Various Carbonyl Groups

Functional Group	Base Position of Carbonyl Absorption ( $\text{cm}^{-1}$ )
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R}' \end{array}$ <p style="text-align: center;">Ketone</p>	1715
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$ <p style="text-align: center;">Aldehyde</p>	1730
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$ <p style="text-align: center;">Carboxylic acid</p>	1710
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OR}' \end{array}$ <p style="text-align: center;">Ester</p>	1740
$\begin{array}{c} \text{O} \qquad \text{O} \\ \parallel \qquad \parallel \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R} \end{array}$ <p style="text-align: center;">Anhydride</p>	1820 and 1750 (two bands)
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{Cl} \end{array}$ <p style="text-align: center;">Acyl chloride</p>	1800
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}_2 \end{array}$ <p style="text-align: center;">Amide</p>	1690–1630 (often has additional bands at slightly lower wavenumbers)

**PRACTICE PROBLEM 13.1**

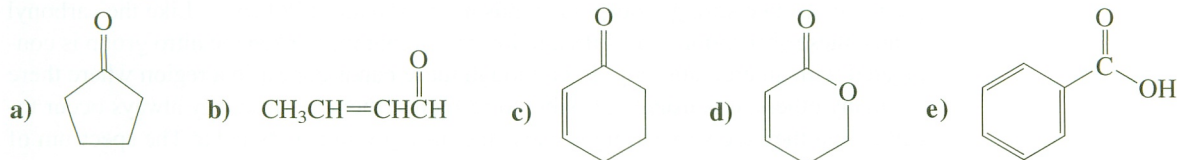
Predict the position of the absorption band for the carbonyl group of this compound in its IR spectrum:

**Solution**

This compound is an ester, and the carbonyl group is conjugated with the aromatic ring. The predicted position is  $1740 - (20 \text{ to } 40) = 1720 \text{ to } 1700 \text{ cm}^{-1}$ .

**PROBLEM 13.8**

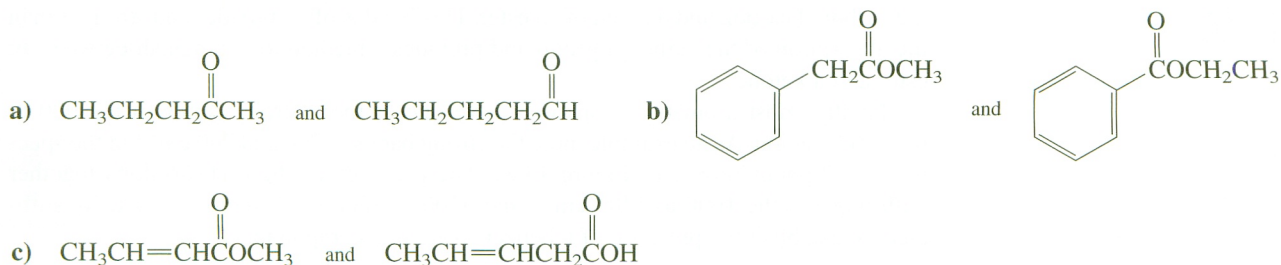
Predict the positions of the absorption bands in the IR spectra for the carbonyl groups of these compounds.



The presence of a carbonyl group in a compound is readily apparent from its IR spectrum. In addition, it is often possible to determine which carbonyl-containing functional group is present from the exact position of the peak *and* an examination of the rest of the spectrum for other absorptions associated with a particular functional group. For example, in addition to a band for the carbonyl group, carboxylic acids have a very broad band in the O—H region, and aldehydes have bands due to the C—H bond in the  $2830 \text{ to } 2700 \text{ cm}^{-1}$  region (see Figures 13.8 and 13.10). Procedures to distinguish among all of these carbonyl-containing functional groups are described in Section 13.10. Remember to check that all the absorptions for a particular functional group appear in the spectrum before deciding that that functional group is actually present in the compound.

**PROBLEM 13.9**

Explain how IR spectroscopy could be used to distinguish between these compounds:





Absorption bands for carbon–nitrogen double bonds occur at somewhat lower wavenumbers than those for carbonyl groups. However, compounds containing this functional group are relatively uncommon, so their IR spectra are not discussed in detail in this book.

Alkenes show an absorption due to the carbon–carbon double bond in the region of 1660 to 1640  $\text{cm}^{-1}$  (see Figure 13.6), which may be shifted to lower wavenumbers because of conjugation. This is a relatively nonpolar functional group, so the absorption band is often weak. Therefore, caution must be used in deciding whether a CC double bond is present in a compound based solely on an absorption in this region. (Look for confirming evidence in the C—H region.) The strength of the absorption increases if the double bond is substituted with a polar group or is conjugated with a carbonyl group.

Aromatic compounds usually show four absorptions due to skeletal vibrations of the benzene ring. These occur near 1600, 1580, 1500, and 1450  $\text{cm}^{-1}$  but vary in intensity (see Figure 13.8). Again caution must be used in assigning these bands, and confirming evidence must be found in other regions of the spectrum before the presence of an aromatic ring can be established.

A final functional group that shows absorptions in this region is the nitro group ( $\text{NO}_2$ ). It has two strong absorption bands near 1550 and 1380  $\text{cm}^{-1}$ . Like the carbonyl bands, these absorptions are shifted to lower wavenumbers when the nitro group is conjugated with an aromatic ring. Even though these bands appear in a region where there are many others, it is usually possible to recognize them because they always occur together and they are very strong because the nitro group is very polar. The spectrum of 2-nitrotoluene is shown in Figure 13.14.

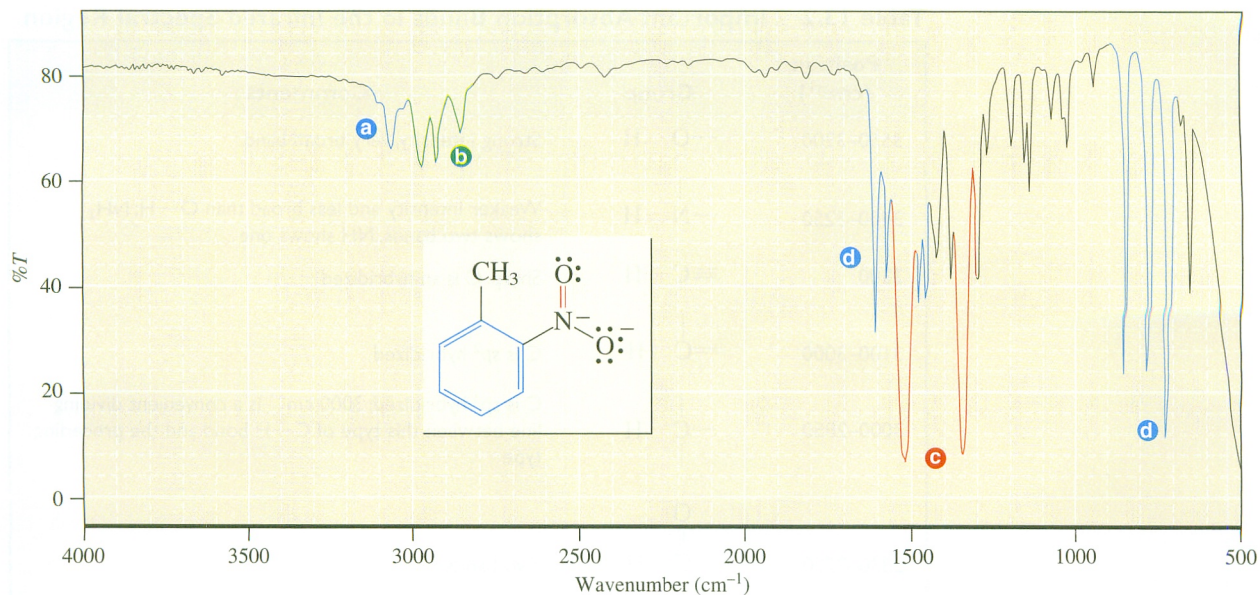
## 13.9 THE FINGERPRINT REGION

The region below 1500  $\text{cm}^{-1}$  contains numerous absorptions due to single-bond stretches and a variety of bending vibrations. Because of the large number of bands, it is difficult to assign these absorptions to a particular functional group. In this book we will make only limited use of this region. However, as its name implies, this is the region where comparison of the spectrum of an unknown to that of a known compound can establish the identity of the unknown. Although the entire spectra must match, the fingerprint region, with its numerous absorptions, provides the crucial test of identity.

One band that is often recognizable in the fingerprint region is the C—O stretch that occurs in the region of 1300 to 1000  $\text{cm}^{-1}$ . This is a strong absorption because the bond is quite polar. Especially useful is the absorption due to the C—O single bond between the carbonyl carbon and oxygen of an ester. This band is often broader and stronger than the absorption of the carbonyl group and provides a method to distinguish between an ester and a ketone.

Finally, most aromatic compounds have one or more strong bands in the 900 to 675  $\text{cm}^{-1}$  region. As an example, note the strong bands at 760 and 700  $\text{cm}^{-1}$  in the spectrum of 2-phenylpropanal (Figure 13.8). The presence of these absorptions together with those in the 1600 to 1400  $\text{cm}^{-1}$  and 3100 to 3000  $\text{cm}^{-1}$  regions is usually sufficient to establish the presence of a benzene ring in a compound.





Two types of CH bonds can be detected in this spectrum:

**a**  $sp^2$ -hybridized CH bonds ( $3100\text{--}3000\text{ cm}^{-1}$ )

**b**  $sp^3$ -hybridized CH bonds ( $3000\text{--}2850\text{ cm}^{-1}$ )

**c** The absorption bands due to the nitro group:  $1523$  and  $1347\text{ cm}^{-1}$ .

They are at lower wavenumbers than usual because the nitro group is conjugated with the benzene ring.

**d** The aromatic ring is responsible for the absorptions due to the  $sp^2$  CH stretching vibrations ( $3100\text{--}3000\text{ cm}^{-1}$ ); the ring skeletal vibrations at  $1612$ ,  $1577$ ,  $1500$ , and  $1461\text{ cm}^{-1}$ ; and the CH bending vibrations at  $859$ ,  $788$ , and  $728\text{ cm}^{-1}$ .

**Nitro compounds:** Compounds containing nitro groups are identified by the appearance of two strong bands near  $1550$  and  $1380\text{ cm}^{-1}$ . These absorptions appear at lower wavenumbers if the nitro group is conjugated with a benzene ring.

**Figure 13.14**

THE INFRARED SPECTRUM OF 2-NITROTOLUENE.

## 13.10 INTERPRETATION OF IR SPECTRA



Interpretation of the IR spectrum of an unknown compound is an art that requires experience and practice. The more spectra you examine, the easier it will become to recognize the absorption due to an O—H group and to differentiate between that band and one that results from an N—H group.

Table 13.2 summarizes the positions of the various absorption bands that have been discussed so far. On the basis of these absorptions, it is usually possible to determine the nature of the functional group that is present in the compound whose spectrum is being considered. Many functional groups require the presence of several characteristic absorptions, whereas the absence of a band in a particular region of the spectrum can often be used to eliminate the presence of a particular group.

Infrared spectra of compounds belonging to each of the major functional group classes are provided in the figures in this chapter. Each figure has a summary of the im-



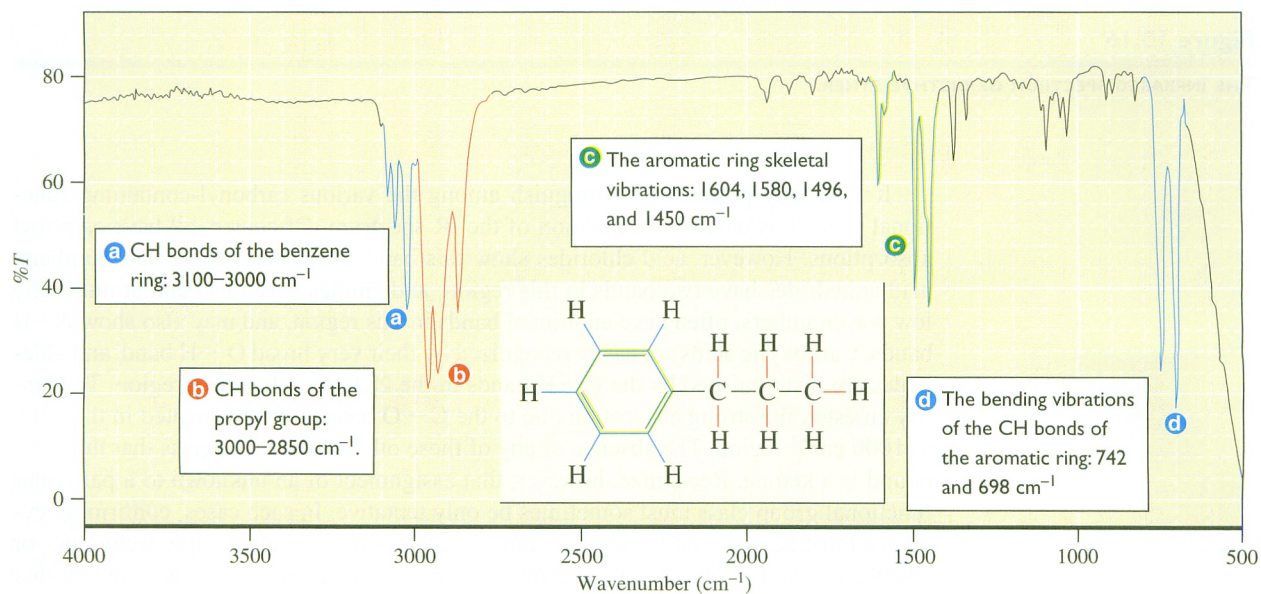
**Table 13.2** Important Absorption Bands in the Infrared Spectral Region

Position (cm <sup>-1</sup> )	Group	Comments
3550–3200	—O—H	Strong intensity, very broad band
3400–3250	—N—H	Weaker intensity and less broad than O—H; NH <sub>2</sub> shows two bands, NH shows one
3300	≡C—H	Sharp, C is sp hybridized
3100–3000	=C—H	C is sp <sup>2</sup> hybridized
3000–2850	—C—H	C is sp <sup>3</sup> hybridized; 3000 cm <sup>-1</sup> is a convenient dividing line between this type of C—H bond and the preceding type
2830–2700	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—H} \end{array}$	Two bands
2260–2200	—C≡N	Medium intensity
2150–2100	—C≡C—	Weak intensity
1820–1650	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \end{array}$	Strong intensity, exact position depends on substituents; see Table 13.1
1660–1640	$\begin{array}{c} \diagup \\ \text{C} \\ \parallel \\ \text{C} \\ \diagdown \end{array}$	Often weak intensity
1600–1450		Four bands of variable intensity
1550 and 1380	—NO <sub>2</sub>	Two strong intensity bands
1300–1000	$\begin{array}{c}   \\ \text{—C—O—} \\   \end{array}$	Strong intensity
900–675		Strong intensity

portant absorption bands for that functional group. Some of these figures are found on previous pages; others appear on later pages. Table 13.3 provides a list of the important functional groups and the figure(s) that show IR spectra of typical compounds containing that functional group. Now that all of the important absorption bands have been discussed, this is a good time for you to examine all of these spectra to become more familiar with the combination of bands caused by each functional group.

**Table 13.3 IR Spectra of Functional Groups**

Functional Group	Figure	Page	Functional Group	Figure	Page
Alkane	13.5	509	Alkene	13.6	510
Alkyne	13.7	510	Arene	13.8	511
Alcohol	13.9	512		13.14	521
Ether	13.16	524		13.15	523
Primary amine	13.11	513		13.18	526
Secondary amine	13.12	514		13.22	529
Tertiary amine	13.17	525	Nitro compound	13.14	521
Ketone	13.4	507	Nitrile	13.13	515
	13.18	526	Aldehyde	13.8	511
Ester	13.19	527	Carboxylic acid	13.10	513
Amide	13.21	528	Anhydride	13.20	528
			Acyl chloride	13.22	529

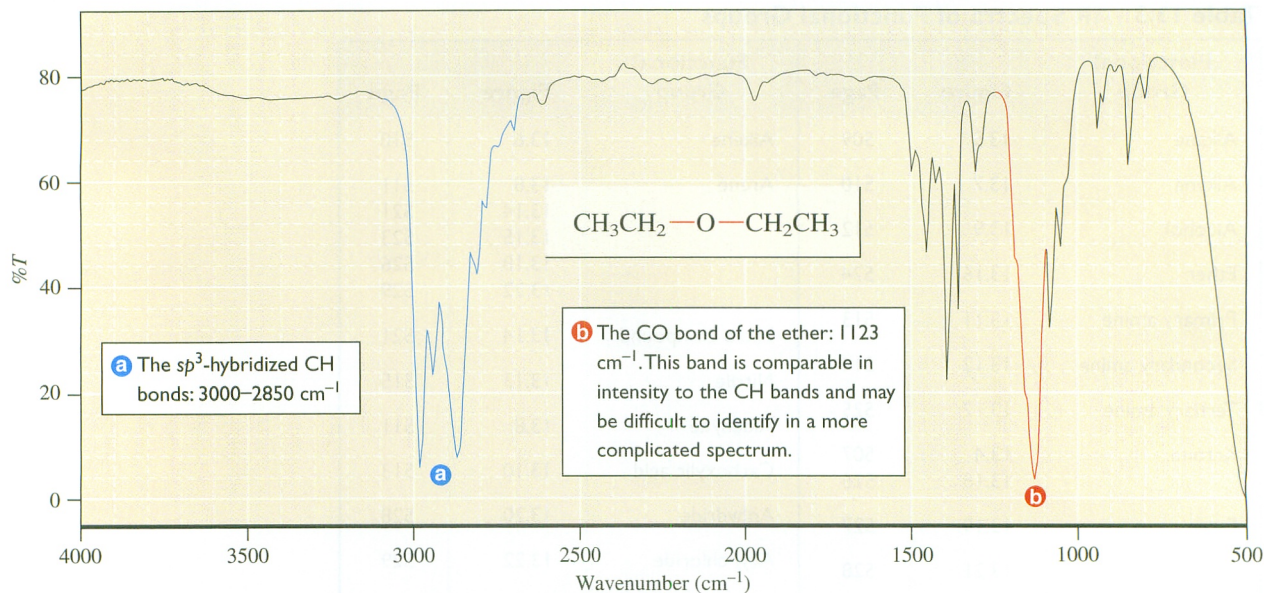


**Arenes:** Arenes that have hydrogens on the aromatic ring show absorptions in the 3100 and 3000 cm<sup>-1</sup> region. They also show four absorptions of variable intensity near 1600, 1580, 1500, and 1450 cm<sup>-1</sup> due to skeletal vibrations of the benzene ring. In addition, most aromatic compounds have at least one strong absorption in the 900 and 675 cm<sup>-1</sup> region due to bending vibrations of the CH bonds of the aromatic ring. Although care must be used in assigning some of these bands because they occur in the fingerprint region, the presence of all of them provides evidence that the compound contains an aromatic ring.

**Figure 13.15**

THE INFRARED SPECTRUM OF PROPYLBENZENE.





**Ethers:** Ethers usually have one or more strong bands in the 1300–1000  $\text{cm}^{-1}$  region due to the C—O bond. As was the case with alcohols, this band is often difficult to identify because it occurs in the fingerprint region with many other absorptions. If oxygen is known to be present from the formula of a compound, the presence of an ether can be inferred by the absence of absorptions due to OH, carbonyl, or other possible oxygen-containing functional groups.

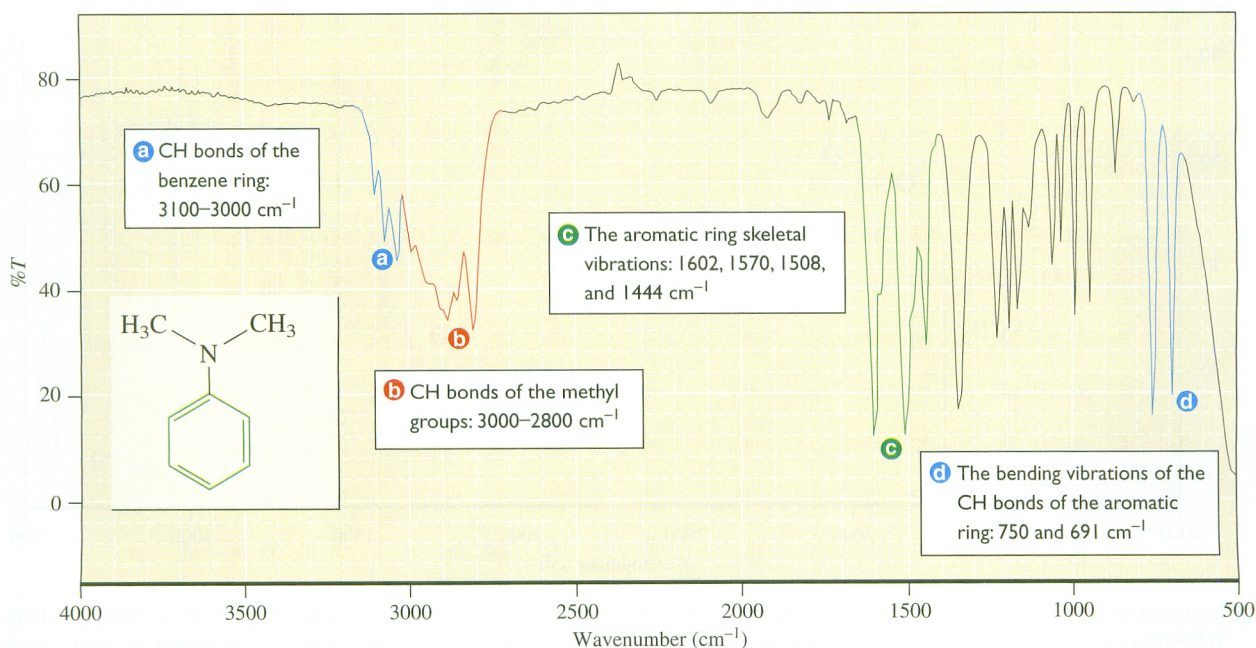
**Figure 13.16**

**THE INFRARED SPECTRUM OF DIETHYL ETHER.**

It is usually possible to distinguish among the various carbonyl-containing functional groups by careful examination of the IR spectrum. Of course, all have carbonyl absorptions. However, acid chlorides show this band at unusually high wavenumbers; acid anhydrides have two bands in this region; and amides have this band at unusually low wavenumbers, often have additional bands in this region, and may also show N—H bands. Carboxylic acids are easily recognized by their very broad O—H band, and aldehydes are distinguished by the C—H bands in the 2830 to 2700  $\text{cm}^{-1}$  region. To identify an ester, the strong absorption due to the C—O bands must be located in the 1300 to 1000  $\text{cm}^{-1}$  region. The absence of any of these other features suggests that the compound is a ketone. Recognize, however, that assignment of an unknown to a particular functional group class must sometimes be only tentative. In such cases, confirming evidence must be obtained from other sources, such as other spectroscopic techniques or chemical tests. Be careful not to become so sure of a functional group assignment that other, contradictory evidence is ignored.

In attempting to identify the functional group that is present in an unknown compound from its IR spectrum, it is usually best to begin by examining the region from 4000 to 2700  $\text{cm}^{-1}$  to determine what type of bonds involving hydrogen are present. Then the region from 2300 to 2100  $\text{cm}^{-1}$  should be examined to look for indications of the presence of triple-bond groups. Next, you should look for absorptions due to carbonyl groups,





Only the alkyl groups and the aromatic ring can be detected in the spectrum of this tertiary amine. The absorptions due to the aromatic ring skeletal vibrations are stronger than usual, suggesting that the ring is substituted with a polar substituent.

**Tertiary amines:** Tertiary amines do not have a NH bond, so there is no evidence for the amine group in the 3400–3250  $\text{cm}^{-1}$  region. Because the CN bond-stretching vibration is difficult to assign in the fingerprint region, tertiary amines are not readily identified from their IR spectra. Chemical tests are helpful in such cases.

**Figure 13.17**

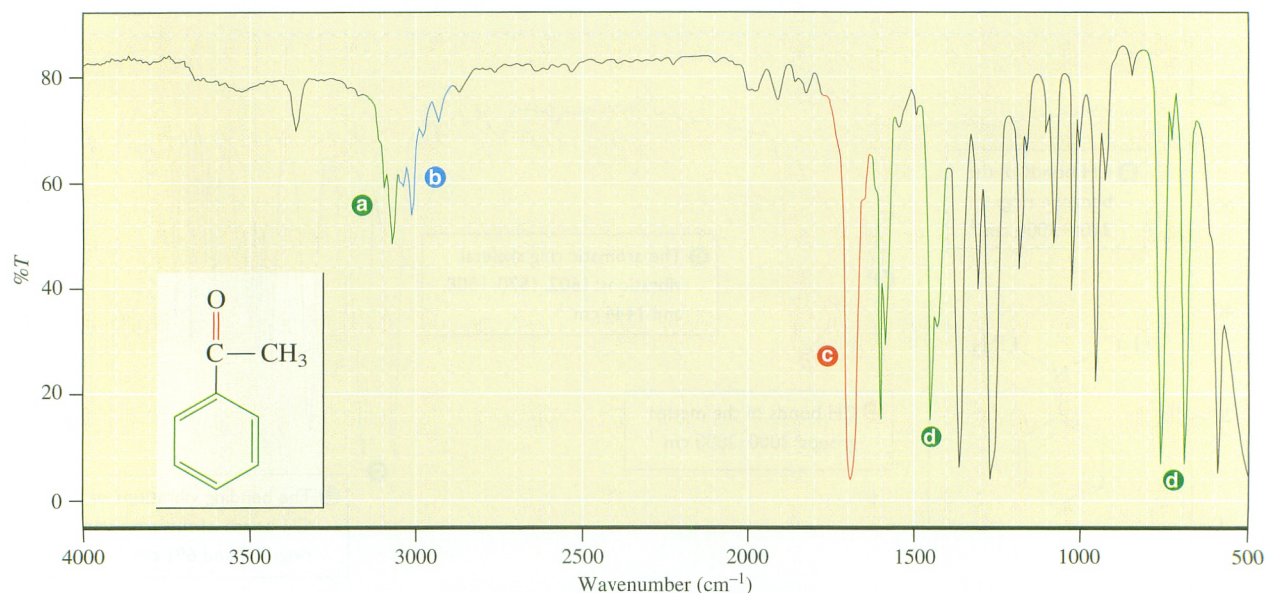
THE INFRARED SPECTRUM OF *N,N*-DIETHYLANILINE.

CC double bonds, aromatic rings, and nitro groups in the 1800 to 1350  $\text{cm}^{-1}$  region. Finally, you should look for C—O absorptions in the 1300 to 1000  $\text{cm}^{-1}$  region and for aromatic ring bands in the 900 to 675  $\text{cm}^{-1}$  region.

Two cautions must be given. First, do not overinterpret the spectrum. Be very careful in assigning the presence of a functional group when only weak bands occur in the appropriate region. It is helpful to compare the spectrum of the unknown to that of a known compound that has that same functional group. Second, make sure that your conclusions are consistent with all of the data. A spectrum that has two bands in the 2830 to 2700  $\text{cm}^{-1}$  region cannot be that of an aldehyde unless it also shows an absorption due to a carbonyl group.

Let's try a problem. The IR spectrum of an unknown compound is shown in Figure 13.23. First, let's examine the hydrogen region. The absence of absorptions in the 3600 to 3100  $\text{cm}^{-1}$  region indicates that the compound does not have any O—H or N—H groups. The bands in the 3100 to 3000  $\text{cm}^{-1}$  region indicate the presence of





**a** CH bonds of the benzene ring:  
3100–3000  $\text{cm}^{-1}$

**b** CH bonds of the methyl group:  
3000–2850  $\text{cm}^{-1}$

**c** The carbonyl group: 1685  $\text{cm}^{-1}$ . This is the position predicted for a carbonyl group of a ketone that is conjugated to an aromatic ring,  $1715 - (20 \text{ to } 40) = 1695 \text{ to } 1675 \text{ cm}^{-1}$ .

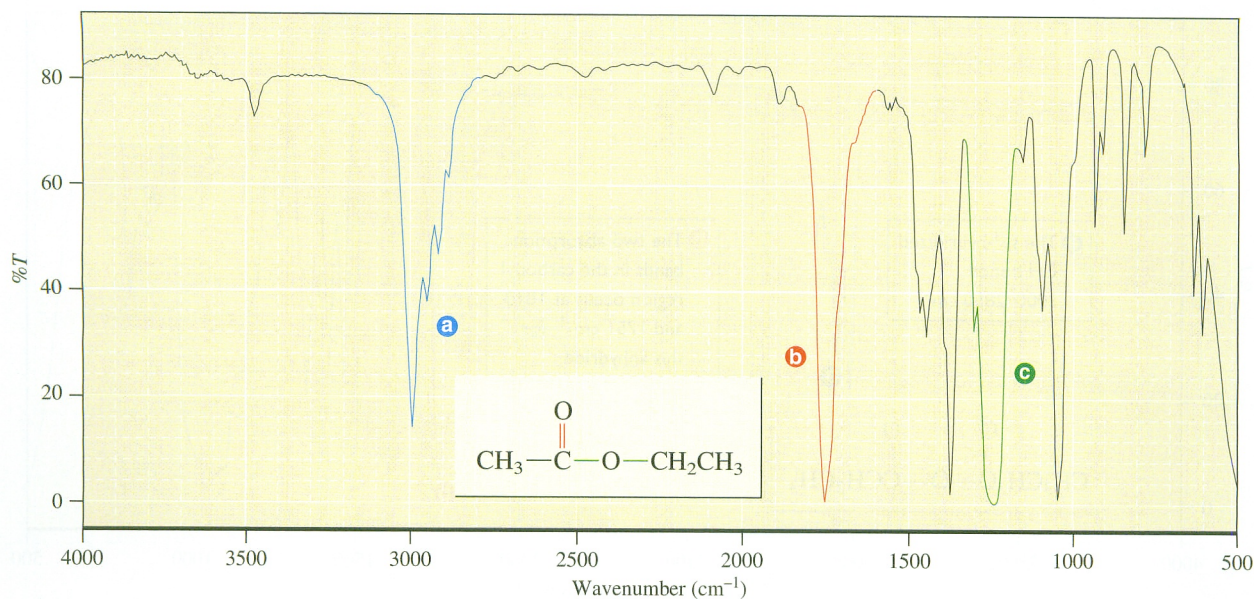
**d** The aromatic ring vibrations: 1599, 1579, 1449, 760, and 691  $\text{cm}^{-1}$ . Note that the band around 1500  $\text{cm}^{-1}$  is very weak in this spectrum.

**Ketones:** The carbonyl of a ketone has an absorption band near 1715  $\text{cm}^{-1}$ . This band is shifted to lower wavenumbers if the carbonyl group is conjugated, and it is shifted to higher wavenumbers if the carbonyl group is part of a five-membered ring. Ketones have no other characteristic bands and often can only be distinguished from the other carbonyl-containing functional groups by the absence of the bands required for those other groups. Again, chemical tests can be very useful in confirming the presence of a ketone.

**Figure 13.18**

THE INFRARED SPECTRUM OF ACETOPHENONE.

hydrogens bonded to  $sp^2$ -hybridized carbons, so the compound must have one or more CC double bonds. The absorptions in the 3000 to 2850  $\text{cm}^{-1}$  region indicate that there are also hydrogens bonded to  $sp^3$ -hybridized carbons in the compound. Next, examination of the triple-bond region shows no indications of the presence of any triple-bonded functional group. Continuing to the double-bond region, the strong absorption at 1722  $\text{cm}^{-1}$  indicates the presence of a carbonyl group. This is not part of a carboxylic acid (no O—H) or an aldehyde (absence of absorptions in the 2830–2700  $\text{cm}^{-1}$  region). Nor does the unknown appear to be an amide (no N—H, carbonyl absorption too high), an anhydride (absence of a second carbonyl band), or an acyl chloride (carbonyl position too low). This leaves a ketone or an ester as possibilities. The strong absorption at 1282  $\text{cm}^{-1}$  suggests that the unknown is an ester. The bands at 1607, 1591, 1489, and 1437  $\text{cm}^{-1}$  along with the absorptions at 3100 to 3000 and 746  $\text{cm}^{-1}$  suggest the presence of an aromatic ring. The carbonyl of the ester



**a** The  $sp^3$ -hybridized CH bonds:  $3000\text{--}2850\text{ cm}^{-1}$

**b** The strong band at  $1742\text{ cm}^{-1}$  is due to the carbonyl group of the ester.

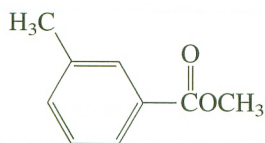
**c** The absorption at  $1241\text{ cm}^{-1}$ , comparable in breadth and intensity to that of the carbonyl group, is due to the CO single bond of the ester.

**Esters:** Esters show a carbonyl band near  $1740\text{ cm}^{-1}$ . They also show a strong absorption in the CO single bond region, from  $1300\text{--}1000\text{ cm}^{-1}$ , that can be used to differentiate them from ketones. This band is usually of comparable breadth and intensity to the carbonyl band. (However, a compound containing both a ketone and an ether group also has both of these absorptions.) Chemical tests can be very useful in distinguishing a ketone from an ester.

**Figure 13.19**

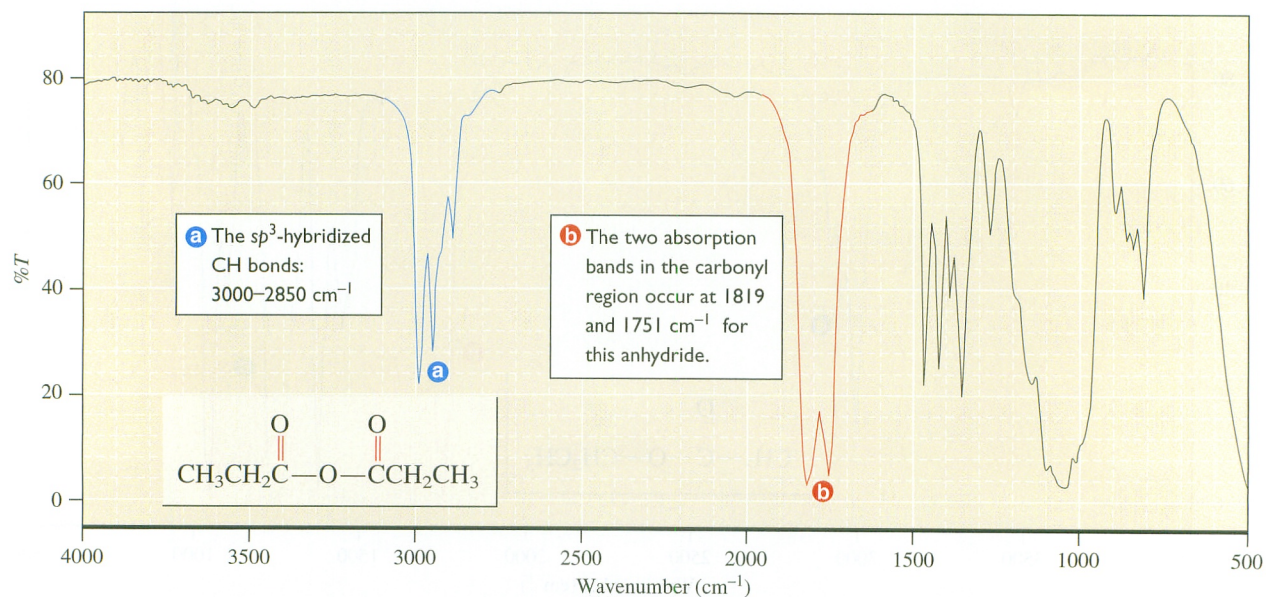
THE INFRARED SPECTRUM OF ETHYL ACETATE.

occurs at slightly lower wavenumbers ( $1722\text{ cm}^{-1}$ ) than the usual position ( $1740\text{ cm}^{-1}$ ), indicating that it might be conjugated. Therefore, we conclude that the unknown is probably an ester, that it may have an aromatic ring, and that the ester may be conjugated (with the aromatic ring?). However, these conclusions must be considered tentative until confirming evidence is obtained from other sources. The unknown is actually methyl 3-methylbenzoate:



Methyl 3-methylbenzoate

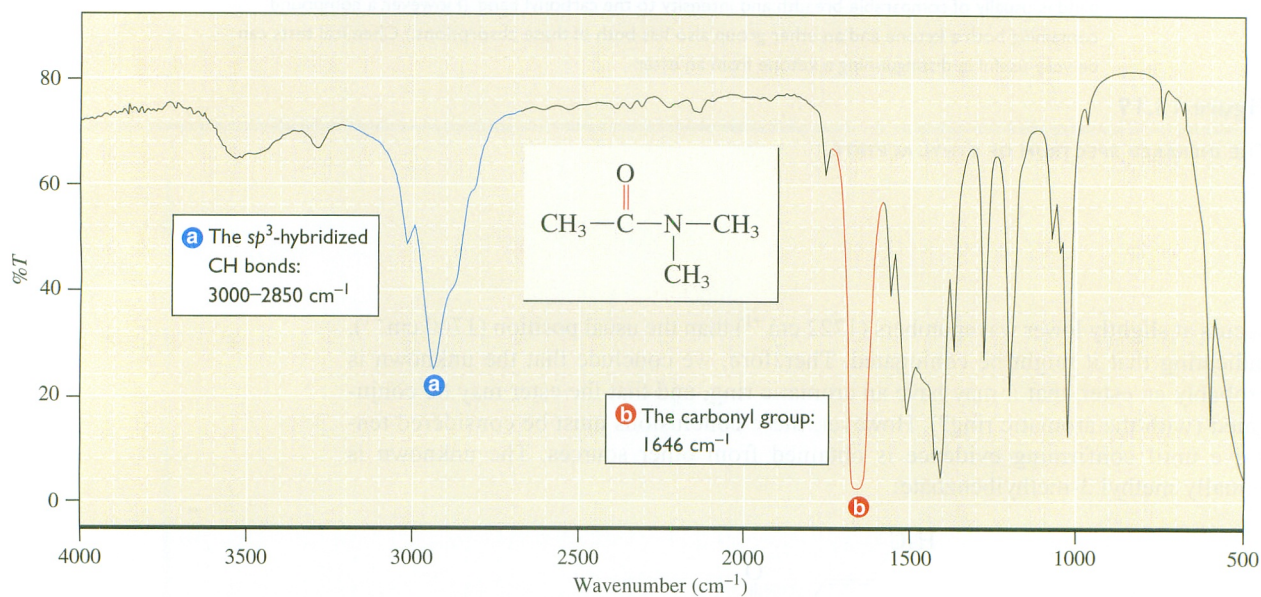




**Anhydrides:** Anhydrides are characterized by the presence of two bands in the carbonyl region, one near 1820 and one near 1750  $\text{cm}^{-1}$ .

Figure 13.20

THE INFRARED SPECTRUM OF PROPANOIC ANHYDRIDE.

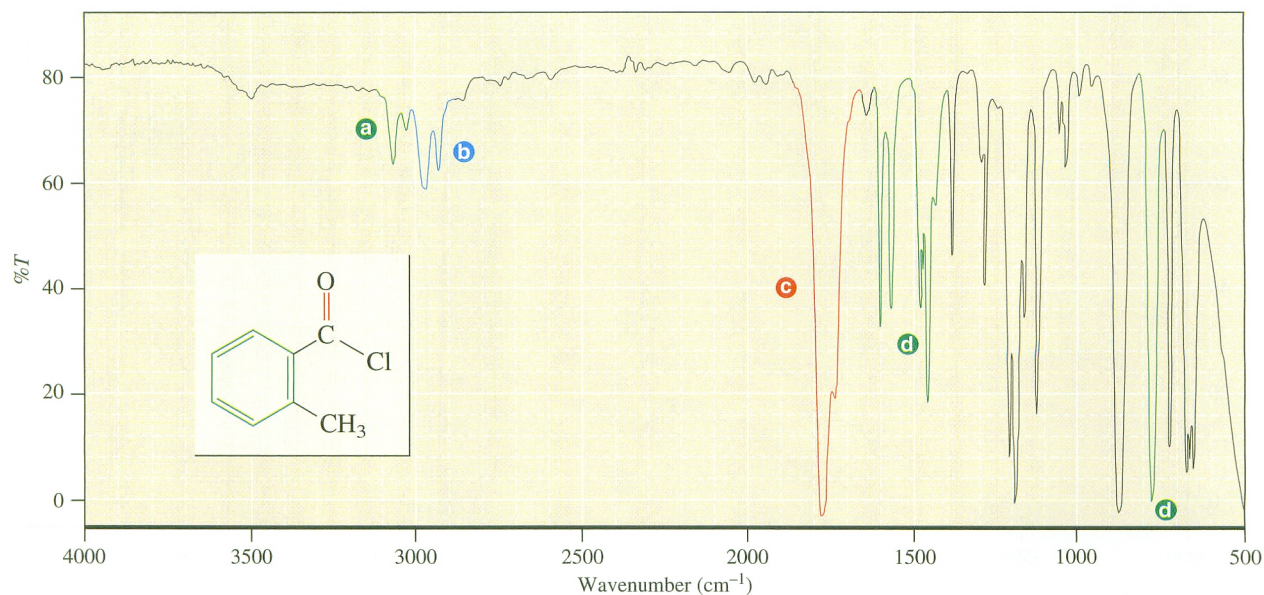


**Amides:** The absorption for the carbonyl group of an amide appears in the region of 1690–1630  $\text{cm}^{-1}$ , lower wavenumbers than most other carbonyl bands. In addition, other relatively strong bands often appear at slightly lower wavenumbers. Amides derived from ammonia or primary amines have bands in the hydrogen region due to their NH bonds.

Figure 13.21

THE INFRARED SPECTRUM OF *N,N*-DIMETHYLACETAMIDE.





**a** CH bonds of the benzene ring:  
3100–3000  $\text{cm}^{-1}$

**b** The  $\text{sp}^3$ -hybridized CH bonds:  
3000–2850  $\text{cm}^{-1}$

**c** The carbonyl group: 1773  $\text{cm}^{-1}$

**d** The aromatic ring: 1601, 1569,  
1478, 1458, and 770  $\text{cm}^{-1}$

**Acyl chlorides:** The carbonyl group of an acyl chloride appears at unusually high wavenumbers, near 1800  $\text{cm}^{-1}$ . Because the carbonyl group is conjugated with the benzene ring in this compound, it is shifted to lower wavenumbers by about 30  $\text{cm}^{-1}$ .

**Figure 13.22**

THE INFRARED SPECTRUM OF O-TOLUYL CHLORIDE.

The exact identity of an unknown cannot be established only on the basis of its IR spectrum (unless, of course, the spectrum of a known exactly matches the spectrum of the unknown). However, information about the functional group that is present in a compound is available. The presence or absence of the following groups can be determined:

O—H

$\text{C}\equiv\text{C}$

Type of  $\text{C}=\text{O}$

$\text{C}-\text{O}$

N—H

$\text{C}\equiv\text{N}$

$\text{C}=\text{C}$

$\text{NO}_2$

Type of C—H

Aromatic ring

The IR spectrum provides little information about the hydrocarbon part of the compound. However, this is exactly the information provided by nuclear magnetic resonance spectroscopy, discussed in Chapter 14. The combination of these two types of spectroscopy is of enormous value in organic chemistry.



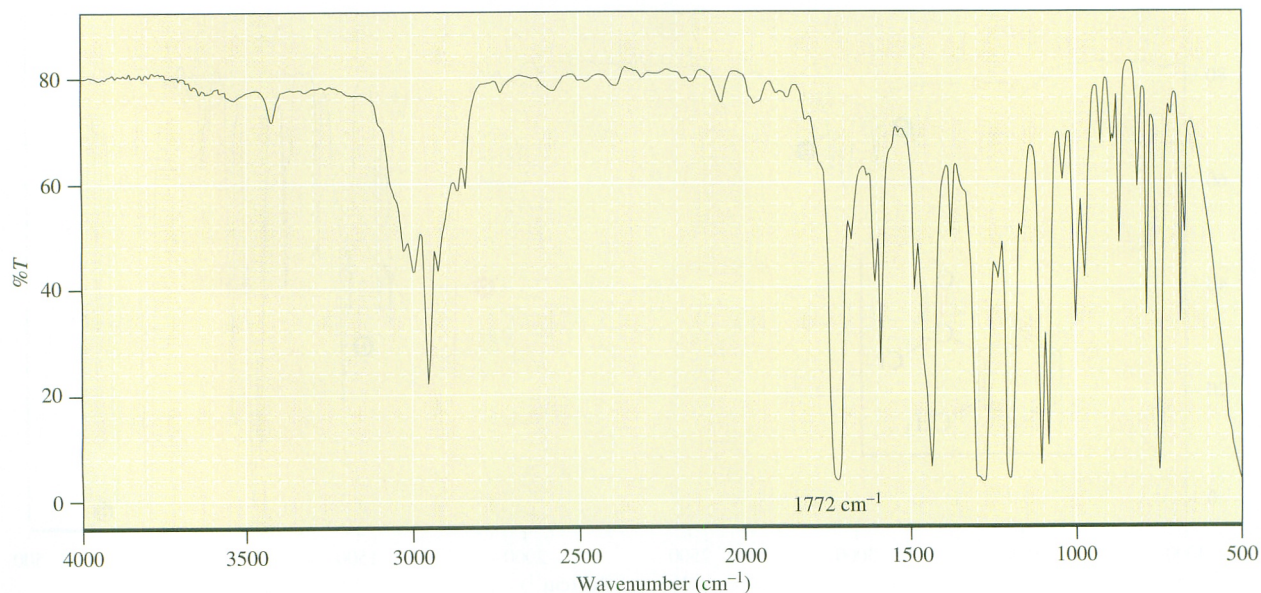
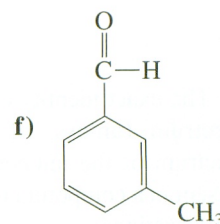
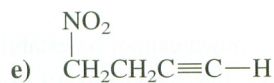
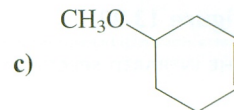
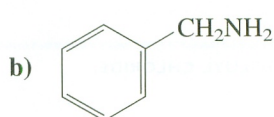
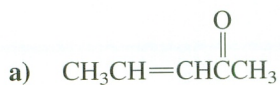


Figure 13.23

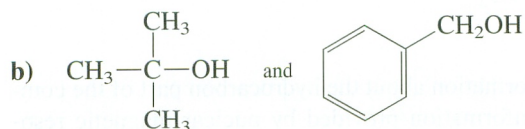
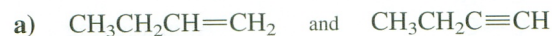
THE INFRARED SPECTRUM OF AN UNKNOWN COMPOUND.

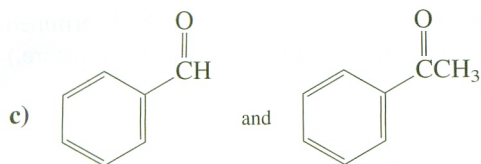
**PROBLEM 13.10**

Predict the positions of the major absorption bands in the IR spectra of these compounds:

**PROBLEM 13.11**

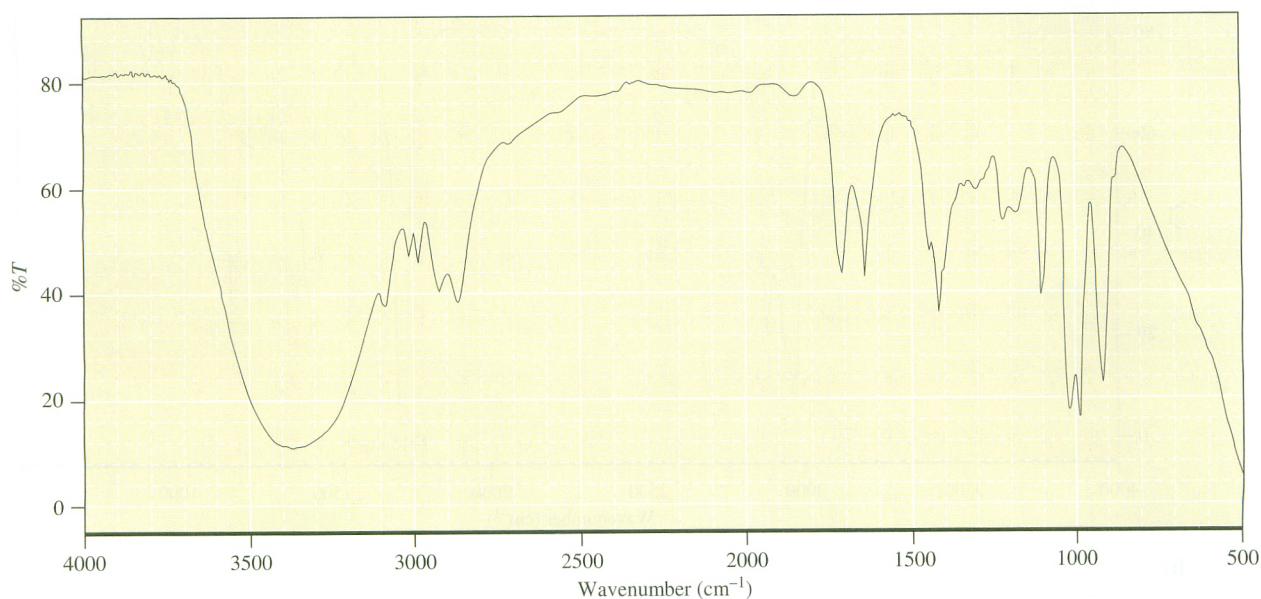
Explain how IR spectroscopy could be used to distinguish between these compounds:





### PRACTICE PROBLEM 13.2

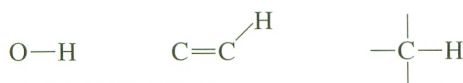
Explain which functional groups are present in this compound on the basis of its IR spectrum:



### Solution

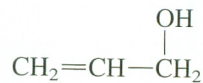
The broad absorption centered near  $3300\text{ cm}^{-1}$  indicates the presence of a hydroxy group. The absorption at  $3005\text{ cm}^{-1}$  suggests the presence of H's bonded to  $sp^2$ -hybridized C's. (Note that you are not expected to read peak positions this exactly from any of these spectra.) This is supported by the absorption for a CC double bond at  $1646\text{ cm}^{-1}$ . The absorptions in the region of  $3000$  to  $2850\text{ cm}^{-1}$  indicate the presence of H's bonded to  $sp^3$ -hybridized C's. Although the compound has a CC double bond, there is no indication of the presence of an aromatic ring due to the absence of the four bands in the  $1600$  to  $1450\text{ cm}^{-1}$  region and the absence of bands in the  $900$  to  $675\text{ cm}^{-1}$  region.

In summary, the structural features that can be identified from the IR spectrum are as follows:





(This is the spectrum of 2-propen-1-ol or allyl alcohol. The structure cannot be determined only from this IR spectrum, but the conclusions reached are consistent with this structure.)



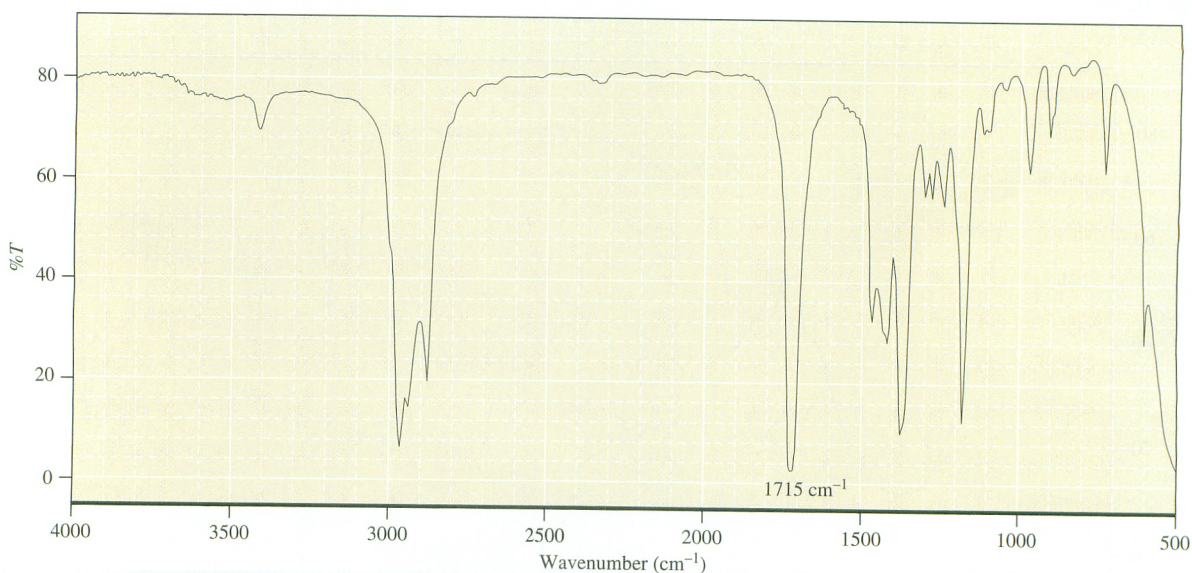
2-Propen-1-ol (allyl alcohol)

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for more practice interpreting  
Infrared Spectra.

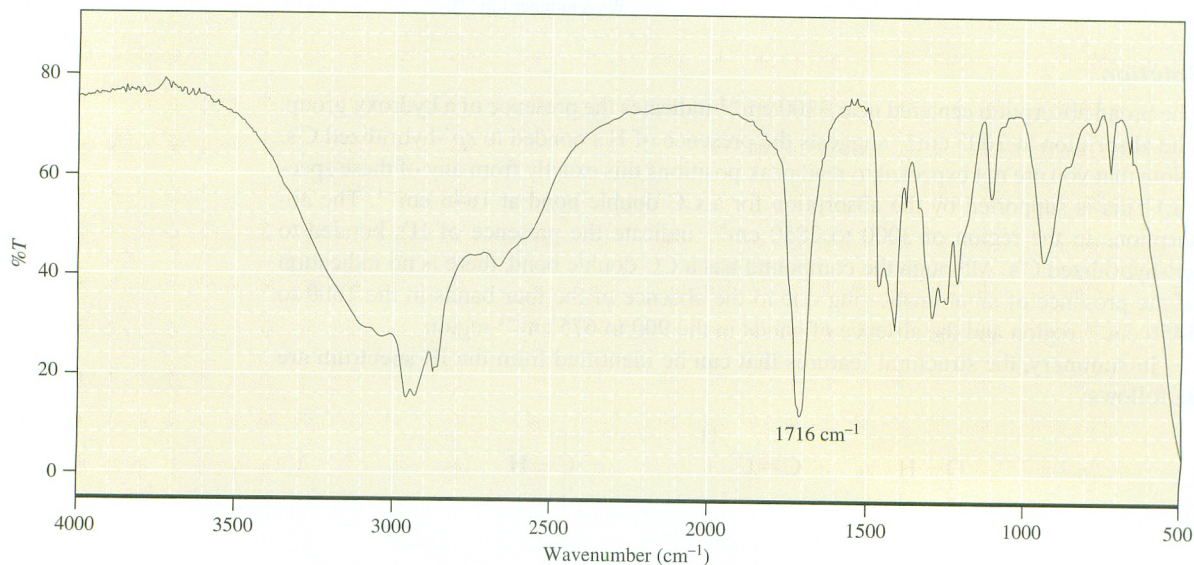
### PROBLEM 13.12

Explain which functional groups are present in these compounds on the basis of their IR spectra:

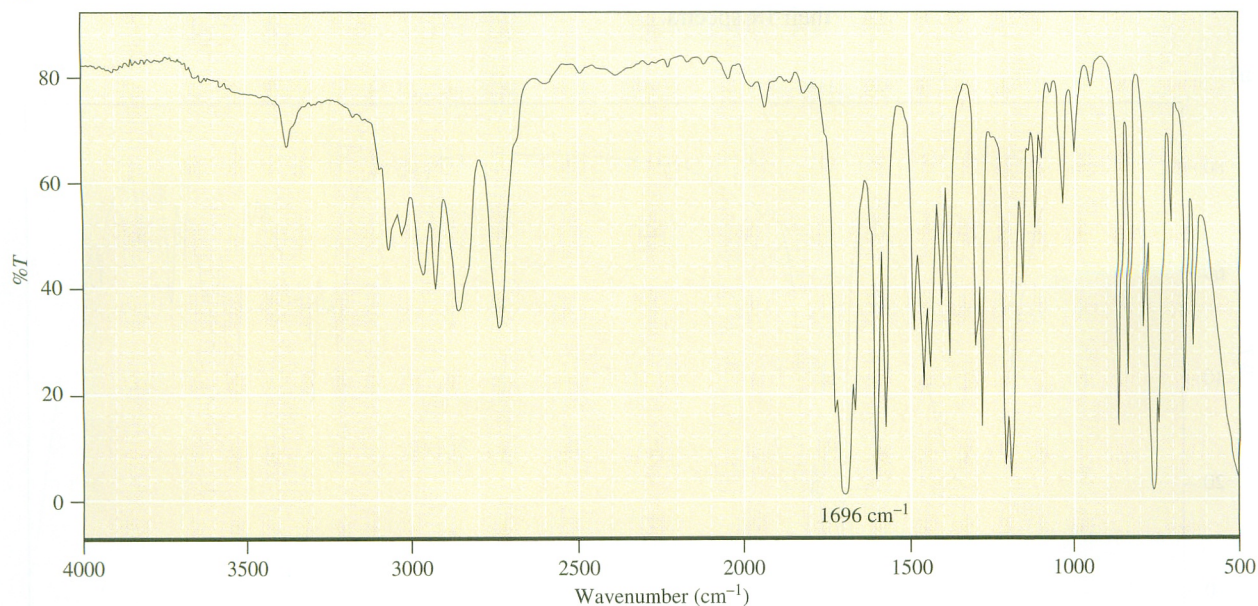
a)



b)



c)



## Review of Mastery Goals

*After completing this chapter, you should be able to:*

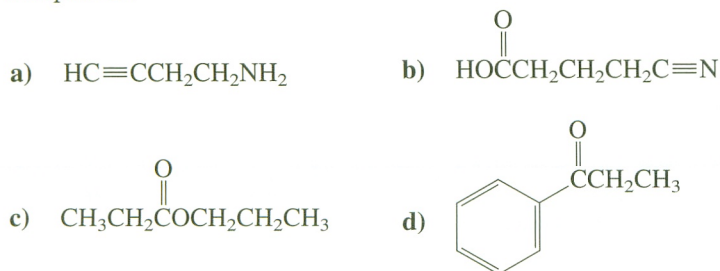
- Predict the important absorption bands in the IR spectrum of a compound. (Problems 13.13, 13.15, 13.26, 13.27, 13.28, and 13.29)
- Determine the functional group that is present in a compound by examination of its infrared spectrum. (Problems 13.14, 13.16, 13.17, 13.18, 13.19, 13.20, 13.21, 13.22, 13.23, 13.24, and 13.25)

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Click *Mastery Goal Quiz* to test how well you have met these goals.

## Additional Problems

- 13.13** List the positions of the important absorption bands in the IR spectra of these compounds:



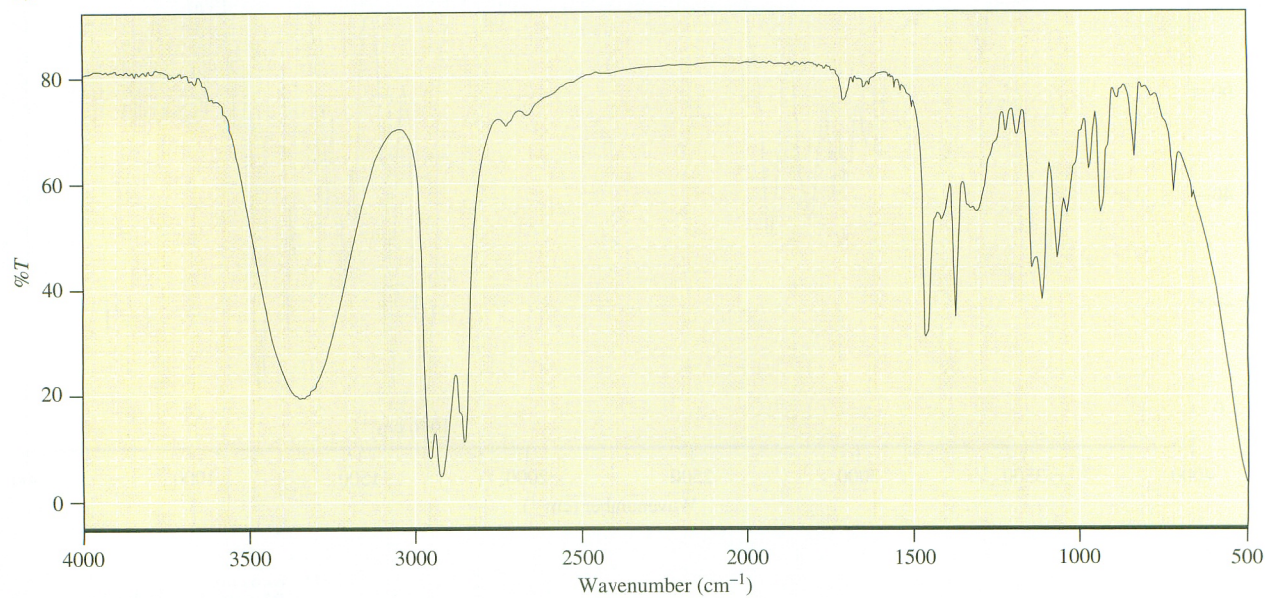
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Assess your understanding of this chapter's topics with additional quizzing and conceptual-based problems at <http://now.brookscole.com/hornback2>

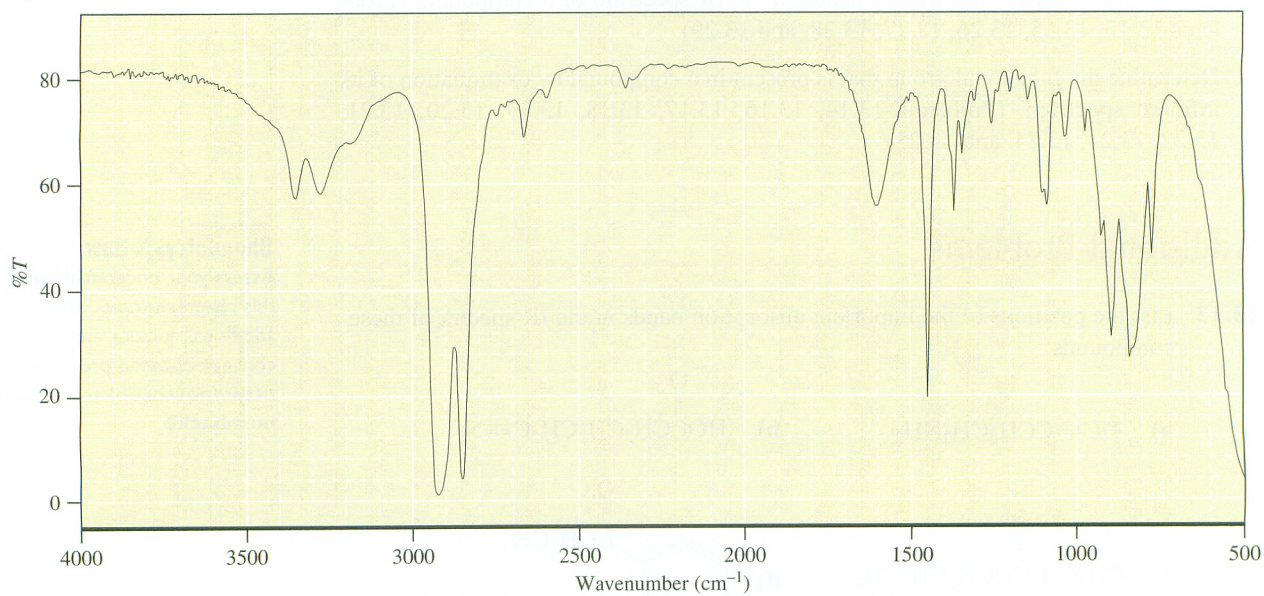


**13.14** Explain which functional groups are present in these compounds based on their IR spectra:

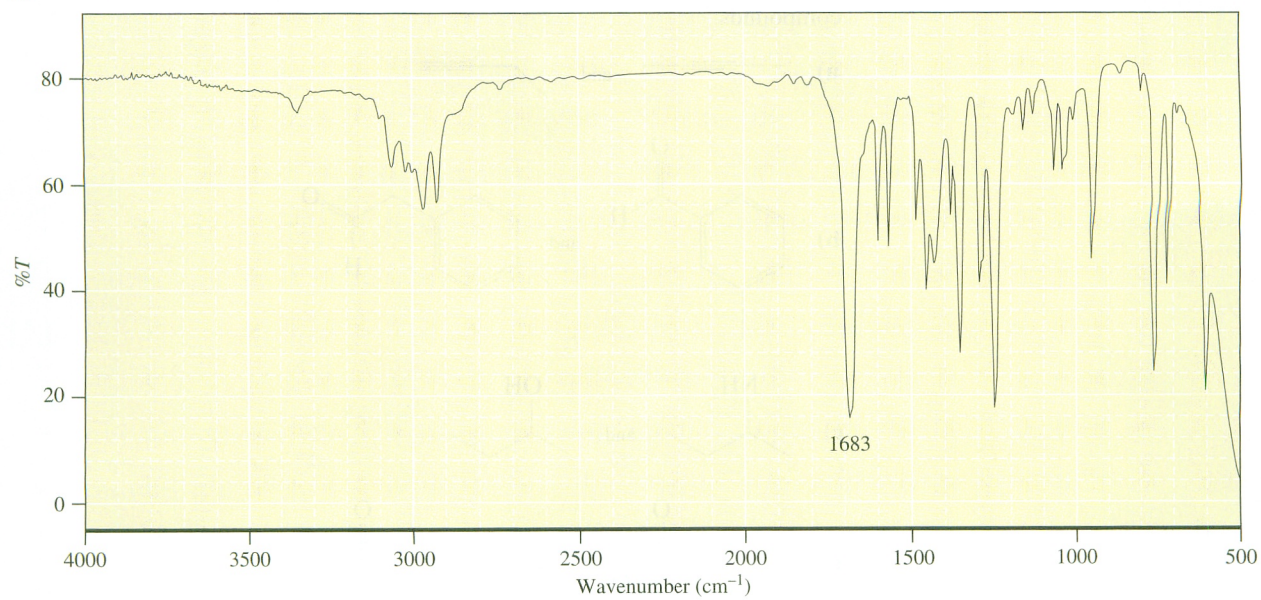
a)



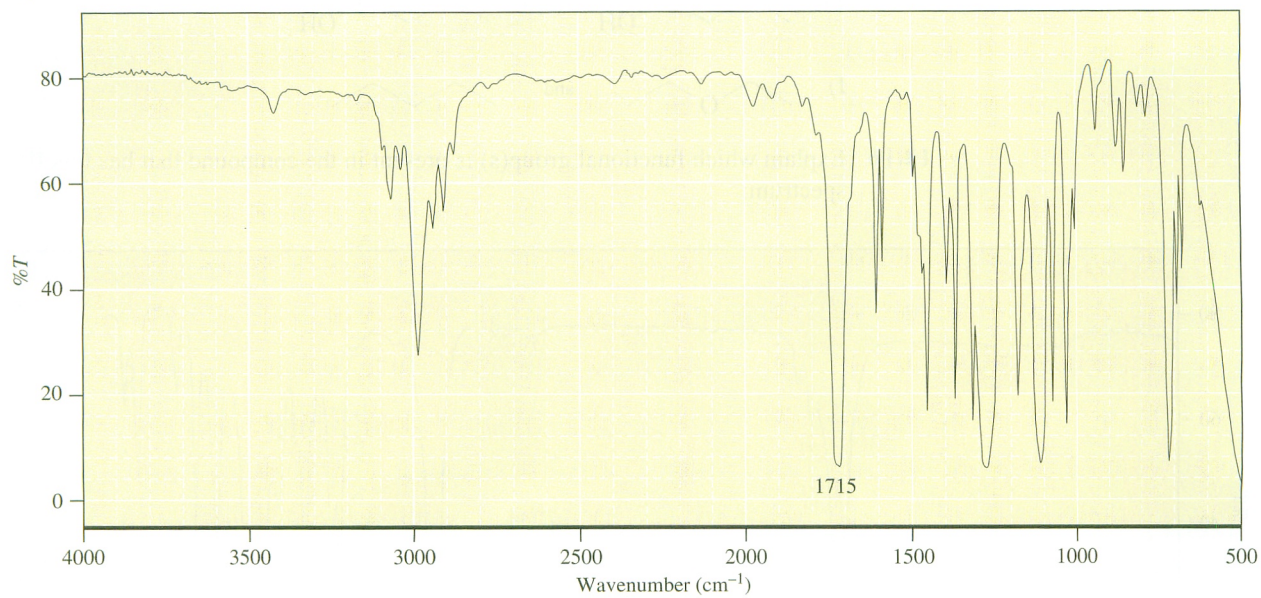
b)



c)

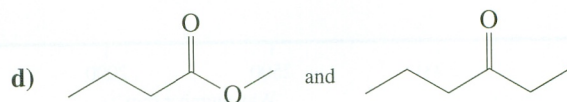
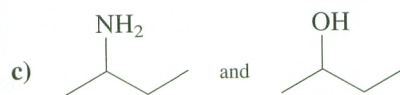
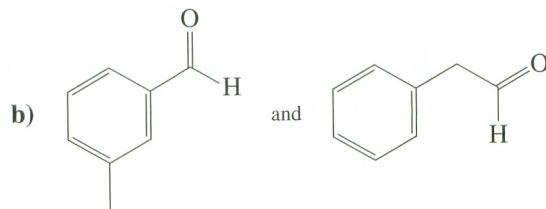


d)

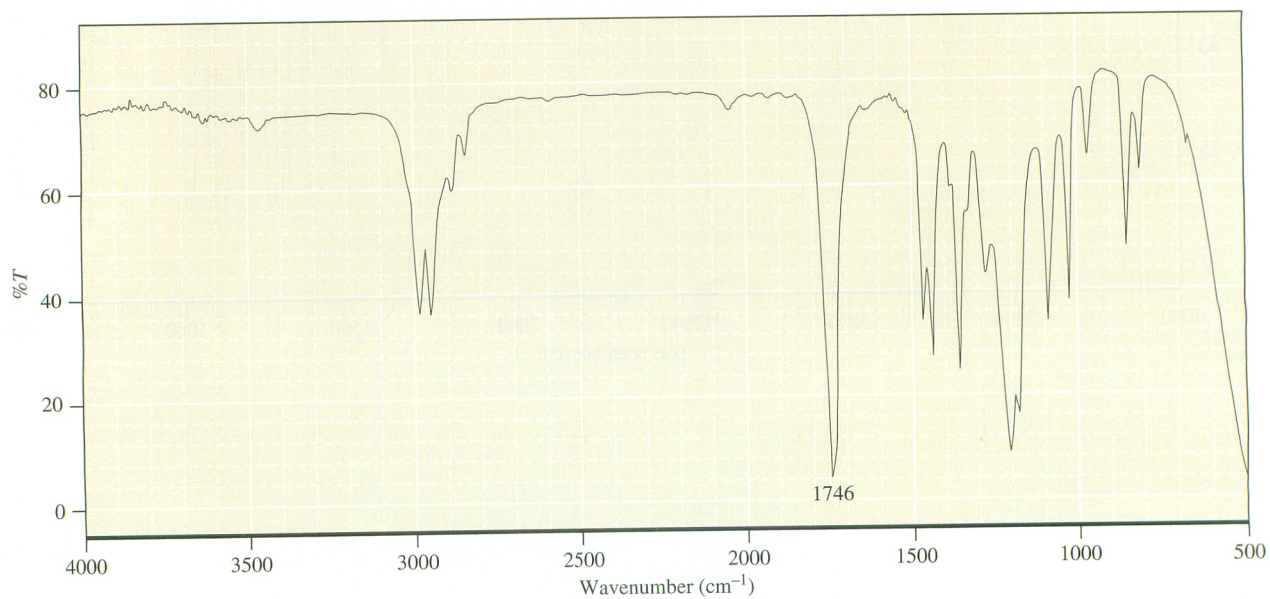




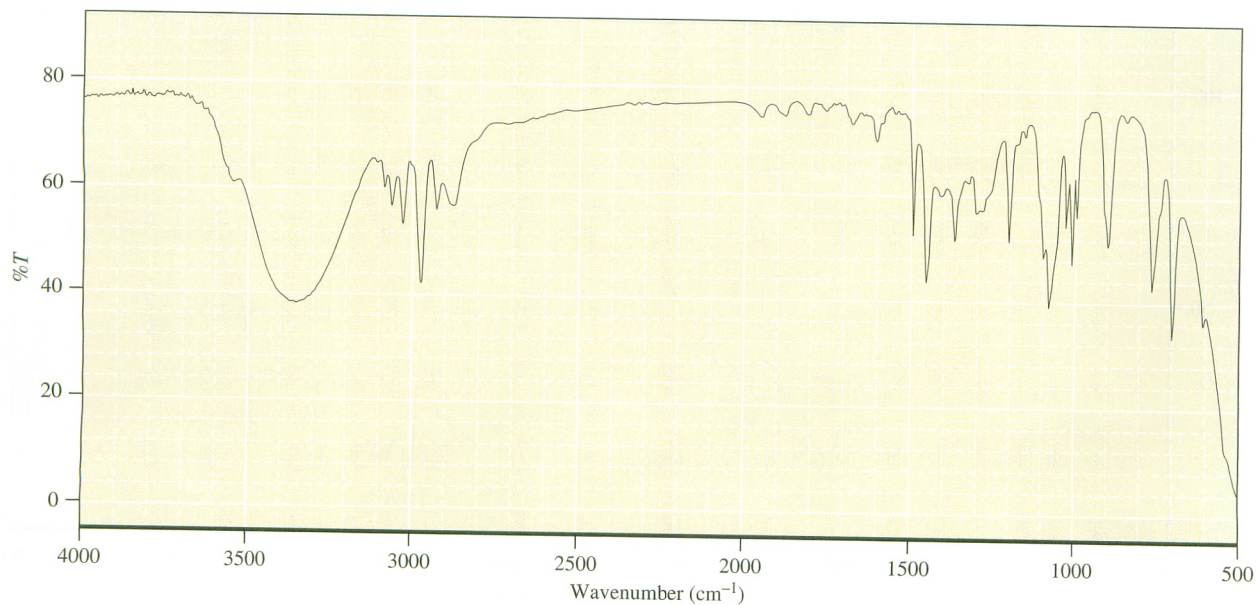
**13.15** Explain how IR spectroscopy could be used to distinguish between these compounds:



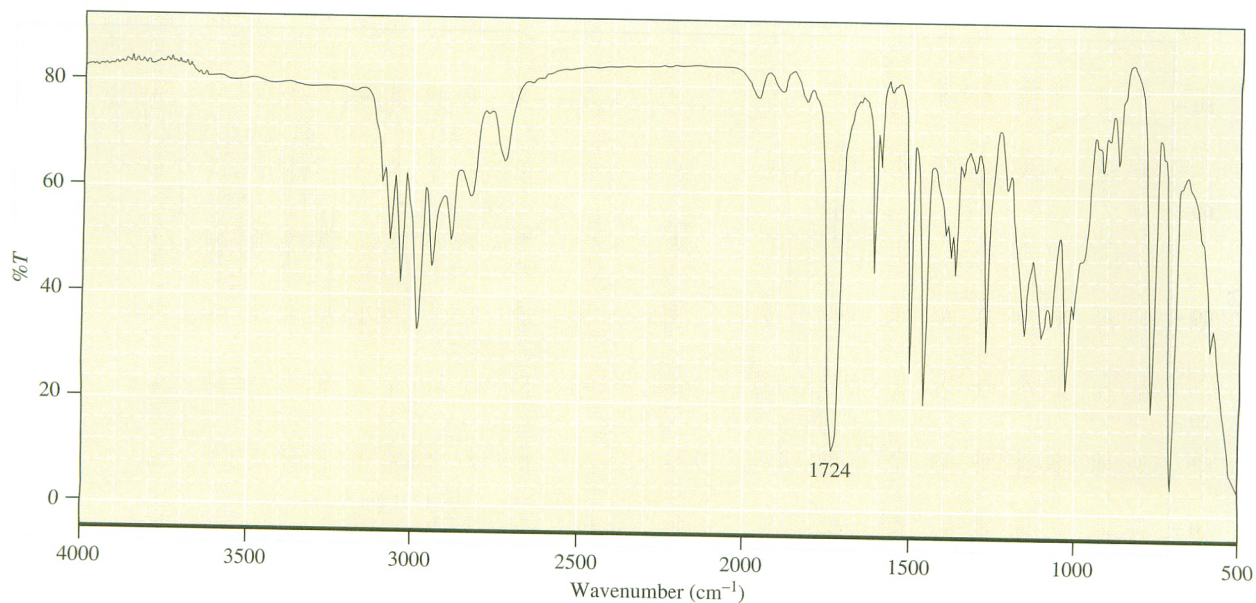
**13.16** Explain which functional group(s) is present in the compound that has this IR spectrum:



**13.17** Explain which functional group(s) is present in the compound that has this IR spectrum:

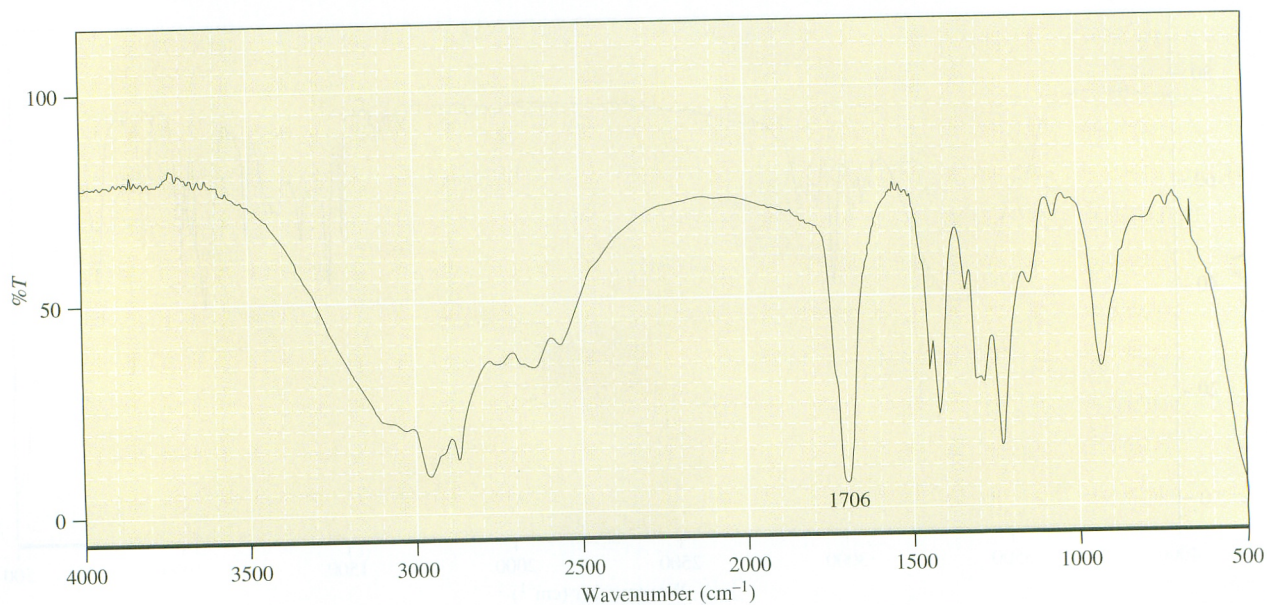


**13.18** Explain which functional group(s) is present in the compound that has this IR spectrum:

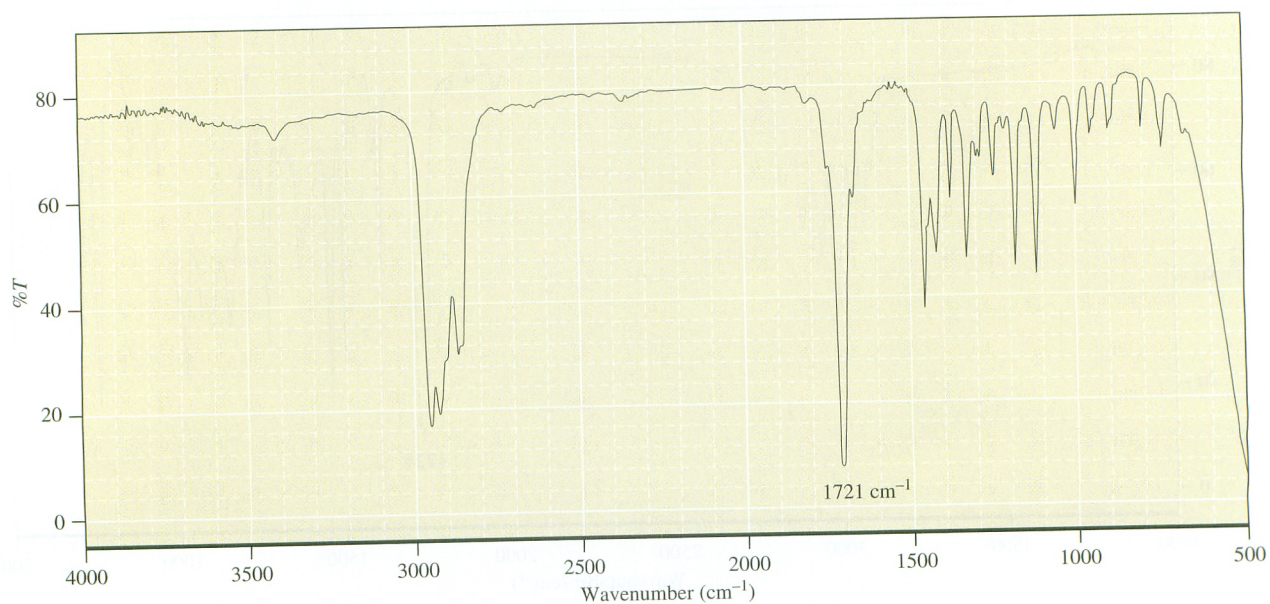




**13.19** Explain which functional group(s) is present in the compound that has this IR spectrum:

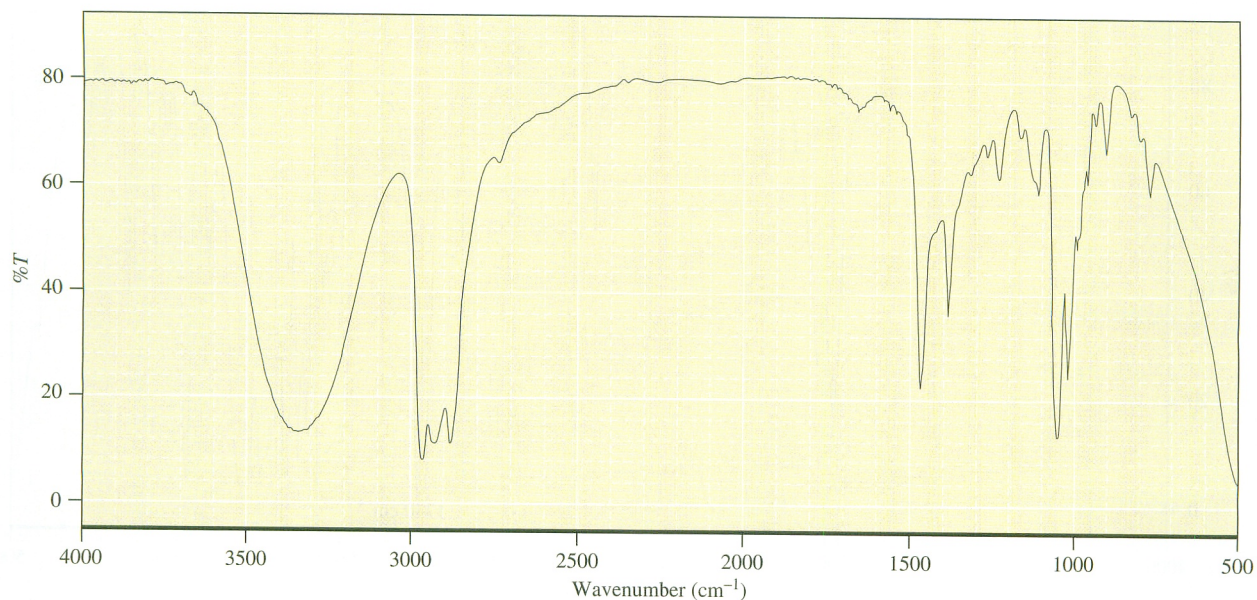


**13.20** Explain which functional group(s) is present in the compound that has this IR spectrum:

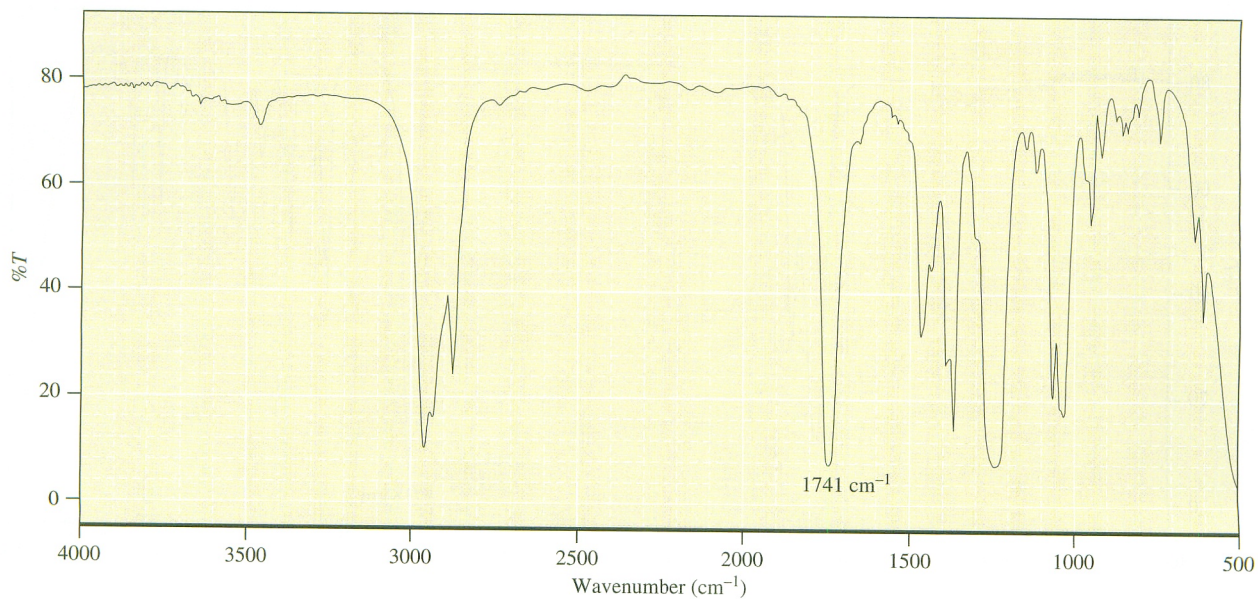




- 13.21** Suggest a possible structure for a compound with the formula  $C_5H_{12}O$  that has the following IR spectrum and explain your reasoning:

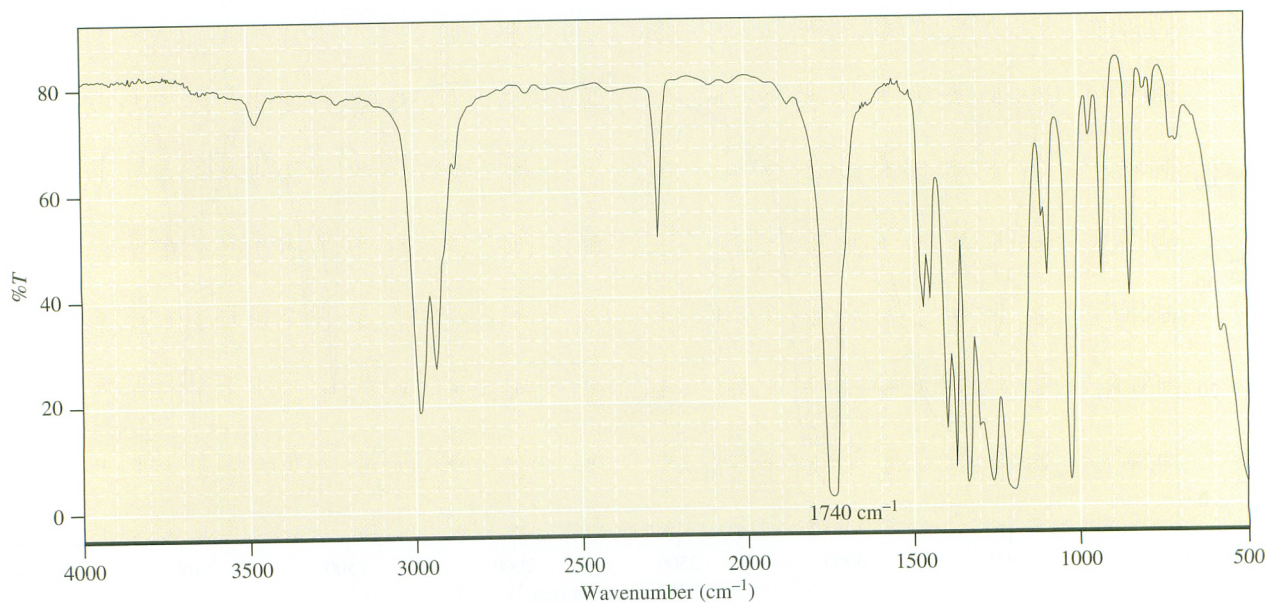


- 13.22** Suggest a possible structure for a compound with the formula  $C_6H_{12}O_2$  that has the following IR spectrum and explain your reasoning:

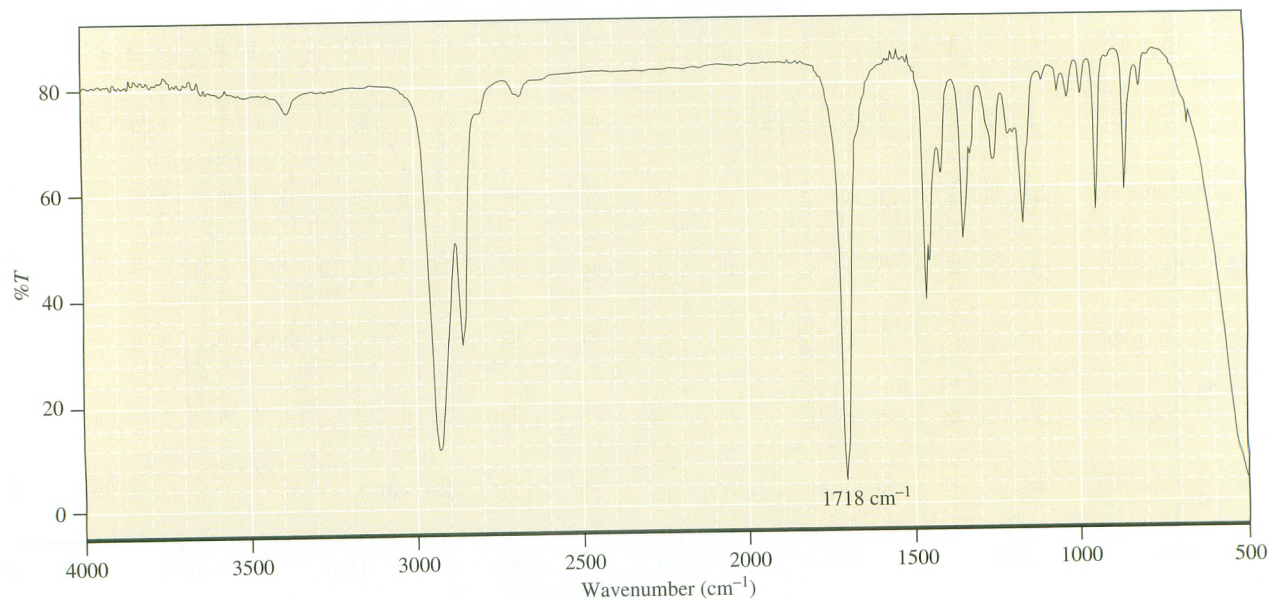




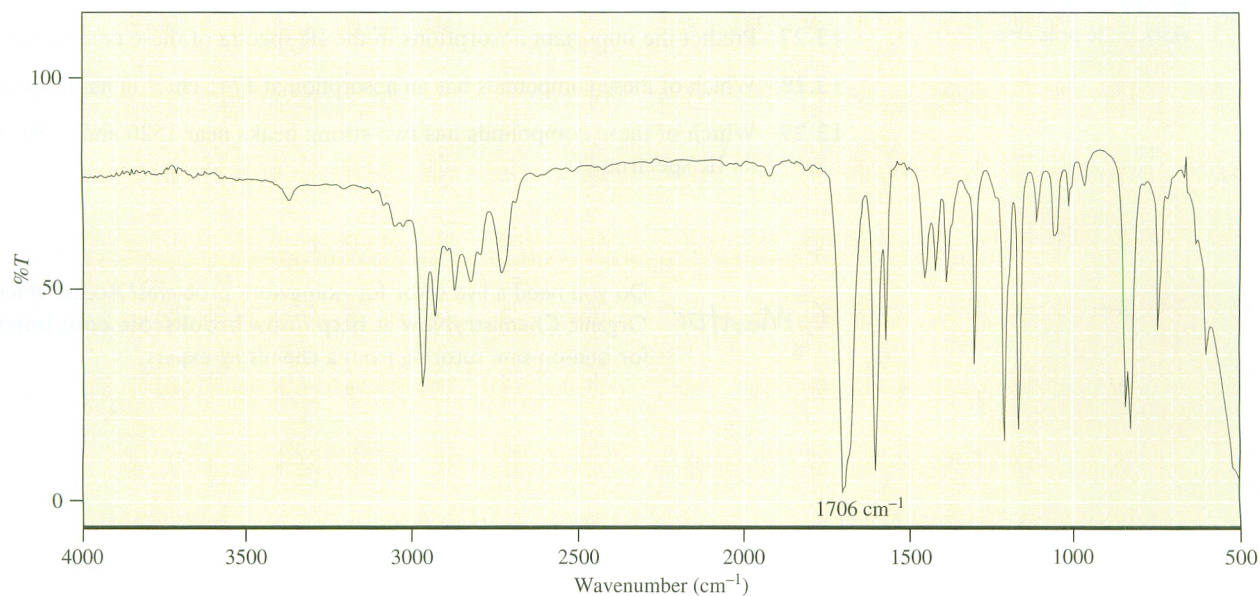
**13.23** Suggest a possible structure for a compound with the formula  $C_5H_7NO_2$  that has the following IR spectrum and explain your reasoning:



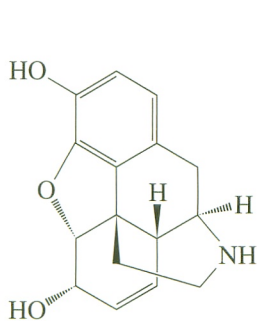
**13.24** Suggest a possible structure for a compound with the formula  $C_7H_{12}O$  that has the following IR spectrum and explain your reasoning:



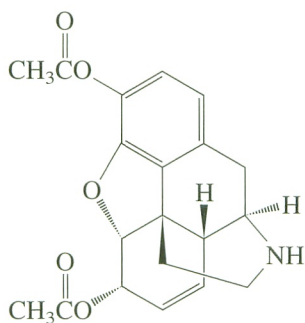
- 13.25** Suggest a possible structure for a compound with the formula  $C_9H_{10}O$  that has the following IR spectrum and explain your reasoning:



- 13.26** Forensic laboratories often have to identify various illicit drug samples. Explain how IR spectroscopy could be used to help distinguish between morphine and heroin.



Morphine



Heroin



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to view the models needed to  
work these problems.

## Problems Using Online Three-Dimensional Molecular Models

- 13.27** Predict the important absorptions in the IR spectra of these compounds.
- 13.28** Which of these compounds has an absorption at  $1741\text{ cm}^{-1}$  in its IR spectrum?
- 13.29** Which of these compounds has two strong peaks near  $1520$  and  $1350\text{ cm}^{-1}$  in its IR spectrum?



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